ADVANCED CHEMISTRY

FOR HIGH SCHOOLS.

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INTRODUCTION.

THIS book is intended to cover the practical work in Chemistry prescribed for the Honor Matriculation and Senior Leaving Examinations. The following is the list of subjects :—

Chemical Theory. The practical study of the following elements, with their most characteristic compounds, in illustration of Mendelejeff's Classification of the Elements : Hydrogen ; Sodium, Potassium ; Magnesium, Zinc ; Calcium, Strontium, Barium ; Boron, Aluminium ; Carbon, Silicon, Tin, Lead ; Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth ; Oxygen, Sulphur ; Fluorine, Chlorine, Bromine, Iodine ; Manganese, Iron. Elementary Qualitative Analysis.

Any study of the elements leading to Mendelejeff's classification is necessarily a comparative one, hence that view of the subject has been kept prominent throughout the book.

Chemical theory has been largely omitted, because teachers will have to give *viva voce* instruction in it anyway, and what may be required beyond that students can get easily and inexpensively in the reference books, which should be in the library of every school in which this class of work is being attempted.

The following books, among others, are desirable ones to have for reference :—

Roscoe and Schorlemmer's Treatise on Chemistry, Vols. I. and II. Macmillan & Co.

Remsen's Chemistry.   Henry Holt & Co.

Bloxam's Chemistry.   Henry C. Lea & Co.

Tilden's Chemical Philosophy.   Longmans & Co.

Muir's Elements of Thermal Chemistry.   Macmillan & Co.

Mixter's Elementary Text Book of Chemistry.   Wiley & Sons.

Ramsay's System of Inorganic Chemistry.   Churchill.

Wurtz' Atomic Theory.   Appleton & Co.

Remsen's Theoretical Chemistry.   Henry C. Lea & Co.

Cooke's New Chemistry.   Appleton & Co.

Richter's Inorganic Chemistry.   Blakiston, Son & Co.

Prescott and Johnston's Qualitative Analysis.   VanNostrand & Co.

Meyer's Modern Theories of Chemistry.   Longmans & Co.

Muir and Slater's Elementary Chemistry.   Cambridge University Press.

Ramsay's Chemical Theory.   Macmillan & Co.

Dobbin and Walker's Chemical Theory.   Macmillan & Co.

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ADVANCED COURSE.

CHAPTER I.

CHLORINE GROUP.

The **halogens** are a group of four elements,—chlorine, bromine, iodine and fluorine, which are very similar to one another in their properties and their compounds. Chlorine has already been studied somewhat in the H. S. Chemistry, so it will not be necessary here to repeat the experiments, or to refer at length to the properties and compounds dealt with in the other book.

1.—Bromine.

EXPERIMENTS.

1. Heat together manganese dioxide and hydrobromic acid, in a test-tube fitted with stopper and delivery tube. Pass the outer end of the delivery tube into a loosely corked bottle containing a little water. *Do not inhale bromine vapour, nor get it on the hands.*

2. Heat bromide of potassium with sulphuric acid and manganese dioxide; collect the vapour that distils over, as in the last experiment.

3. Drop a little bromine solution on starch paste. Does vapour of bromine produce a similar effect?

The reactions in the foregoing experiments are similar to the corresponding ones in the case of chlorine. The equations may be written from the analogous chlorine ones by changing the symbol Cl to Br. The following experiment is to determine the relative combining powers of chlorine and bromine.

4. Drop some chlorine water into a solution of hydro-bromic acid, or a colourless solution of any other bromide. Try the effect of the bromide on starch paste, both before and after the chlorine has been used. Reverse the process by dropping bromine water into a solution of chloride, then testing for free chlorine.

5. Vapourize some bromine in a flask, then lower into it a bit of phosphorus ; drop in a little water and after the fumes have been dissolved test for acid properties.

6. Try if bromine solution will bleach coloured cotton, writing ink, pencil marks, logwood solution and magenta solution.
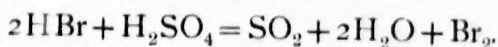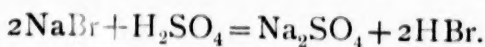

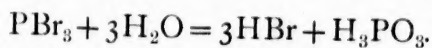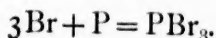## 2.—Hydrobromic Acid.

EXPERIMENTS.

1. Heat a mixture of sulphuric acid and a bromide. Pass the gas that comes off into litmus solution. Is it soluble ?

2. Drop into some hydrobromic acid solution a little sulphuric acid. Test for free bromine.

Explanation.—These two experiments show one difference between chlorine and bromine. When a chloride is heated with sulphuric acid, hydrochloric acid gas results; when a bromide is similarly treated, free bromine is formed. Since hydrobromic acid is decomposed by sulphuric acid, it follows that though the bromide may be decomposed hydrobromic acid will not be formed in presence of free sulphuric acid.

$$2NaBr + H_2SO_4 = Na_2SO_4 + 2HBr.$$
$$2HBr + H_2SO_4 = SO_2 + 2H_2O + Br_2.$$

The different results in the cases of chlorine and bromine may be accounted for by the greater chemical attraction between hydrogen and chlorine than between hydrogen and bromine. It is evident then that hydrobromic acid must be prepared by some method in which free sulphuric acid will not be used. The way in which this is done is by allowing bromine to drop very slowly on phosphorus in presence of water.

$$3Br + P = PBr_3.$$
$$PBr_3 + 3H_2O = 3HBr + H_3PO_3.$$

The phosphorus tribromide decomposes the water to form hydrobromic and phosphorous acids. The former may be driven off in vapour by heat, and dissolved in cold water.

3. Pass a current of sulphuretted hydrogen into a solution of bromine

$$H_2S + Br_2 + H_2O = 2HBr + H_2O + S$$
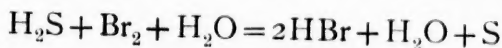
3.—Iodine.

EXPERIMENTS.

1. Heat a mixture of an iodide with manganese dioxide and sulphuric acid. The vapour that comes off may be collected in an empty bottle. Is it soluble?

2. Heat some manganese dioxide with hydriodic acid Compare the corresponding reactions under chlorine and bromine.

3. Heat a little iodine in a test-tube, observe the vapour and its condensation.

4. Add a very small bit of iodine to some starch paste.

5. Place a shaving of phosphorus on a metal plate and lay on the phosphorus a little iodine.

6. Drop a bit of iodine into a test-tube half full of water. After shaking for some time notice the colour, then drop into the solution a crystal of iodide of potassium, and again shake.

7. Try the solubility of iodine in alcohol, chloroform, and bisulphide of carbon.

8. Make a thin mucilage by boiling starch in plenty of water. Pour a little of this into each of three test-tubes. To the first add a drop or two of a very weak aqueous solution of iodine, to the second and third a few drops of solution of an iodide; then into the second pour a few drops of bromine solution, and into the third a little chlorine solution.

4.—Hydriodic Acid.

EXPERIMENTS.

1. Add a shaving of phosphorus to some iodine solution in a test-tube, heat, pass the gas that comes off into cold water, and test both the gas and its solution for acid properties, also test it for free iodine and for an iodide. Compare the reaction when hydrobromic acid was prepared.

2. Place a shaving of phosphorus on a metal plate, and heap some powdered iodine on it (use excess of iodine). Invert a beaker over the mass, and after chemical action has ceased, quickly slip a glass plate under the mouth of the beaker, and shake the fumes which it contains with a little water. Test, as in ex. 1.

3. Pass a current of hydrogen sulphide through a solution of iodine until the latter is decolourized $I_2 + H_2S = 2HI + S$. Test, as in ex. 1.

Allow a portion of this solution to stand exposed to air for a few days, then repeat the test.

4. To prepare hydriodic acid gas in quantity, put a little red phosphorus in a tube and twelve times as much (by weight) powdered iodine ; heat gently, until a dark coloured mass is formed. Let water fall, a drop at a time, on this mass. Pass the gas that comes off into cold water. Collect a tube full of the gas and heat it.

5.—Notes on the Halogens.

Fluorine.—When calcic fluoride (fluor spar) CaF_2 is warmed with sulphuric acid it yields hydrofluoric acid,—

a colourless gas, soluble in water and active chemically. It is chiefly of use because it attacks glass, forming silicon fluoride, SiF_4. The acid may be easily prepared by heating the fluor spar with strong sulphuric acid, and it may be condensed in a freezing mixture in a lead tube.

Fluorine has been prepared by the electrolytic decomposition of anhydrous hydrofluoric acid, kept at a temperature at which it is in the liquid form. It is a colourless gas that unites with great energy with most elements. It decomposes water, setting free oxygen in the form of ozone. Phosphorus, antimony, boron and sulphur take fire in it. With most metals it forms fluorides, and even gold and platinum are attacked by it when heated. It does not unite directly with oxygen, nitrogen or carbon ; and no compound of fluorine and oxygen has been obtained by reduction of other compounds.

Hydrogen fluoride, HF, is a very weak acid, hence fluorides are not plentiful, that of calcium being the best known. Double fluorides, such as $KFHF$, BiF_33HF are not uncommon. They generally consist of a metallic fluoride joined with that of hydrogen.

6.—Occurrence and Preparation.

Chlorine is found generally distributed in nature in combination with other elements. Bromine, in the form of bromides, occurs in the waters of many mineral springs, in some salt beds, accompanying chlorides, and with iodine in sea weeds. Iodine is found in sea weeds that are largely collected on the north-western shores of

Europe. These plants are burned, the soluble salts dissolved out of the ashes, and the iodine and bromine separated by the use of sulphuric acid and manganese dioxide. The iodine passes off first and is collected on the sides of cold vessels. Afterwards, by similar treatment the bromine is obtained. Fluorine is found in mineral form as calcium fluoride (fluor spar), and cryolite, sodium fluoride.

7.—Compounds of the Halogens.

The compounds of chlorine, bromine and iodine are similar in their properties, and are generally prepared by similar methods. The hydrogen compounds offer a partial exception to this last statement, because hydrobromic and hydriodic acids break up in presence of sulphuric acid to form free bromine or iodine, sulphur dioxide and hydrogen sulphide.

When chlorine is passed into solution of caustic potash a mixture of the chloride and the chlorate of potassium is formed (H. S. Chem., page 161). When bromine or iodine is passed into caustic potash solution a reaction occurs according to the following equation :

$$3M_2 + 6KHO = 5MK + KMO_3 + 3H_2O$$

when M = either Br. or I.

The following is a tabulated statement of some of the commonest non-metallic compounds of these halogens :

CHLORINE.	BROMINE.	IODINE.
HCl	HBr	HI
HClO	HBrO	————
$HClO_2$	————	————

CHLORINE.	BROMINE.	IODINE.
$HClO_3$	$HBrO_3$	HIO_3
$HClO_4$	$HBrO_4$?	HIO_4
Cl_2O	———	———
ClO_2	———	———
———	———	I_2O_5
S_2Cl_2	S_2Br_2	S_2I_2
SCl_2	———	———

Chloric acid is prepared by acting on a chlorate, generally of barium, with sulphuric acid. It is very unstable and readily decomposes into hydrochloric acid, oxygen and perchloric acid, thus :

$$4HClO_3 = 2HClO_3 + 2HCl + 3O_2$$
$$= 2HClO_4 + 2HCl + 2O_2.$$
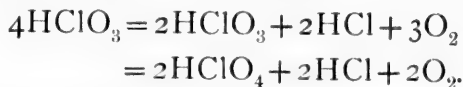
The perchloric acid, $HClO_4$, is much more stable, is not decomposed by sulphuric acid, and forms hydrated acids of the composition $H_3ClO_5 = HClO_3(H_2O)$, $H_5ClO_6 = HClO_3(H_2O)_2$.

Bromic acid is obtained from the action of chlorine on bromine solution,

$$5Cl_2 + Br_2 + 6H_2O = 2HBrO_3 + 10HCl.$$
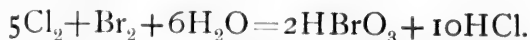
Iodic acid may be obtained by decomposing an iodate or by oxidizing iodine. If iodine be boiled with strong nitric acid, the following reaction occurs :

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

Periodic acid, HIO_4, is known only from its salts.

Chlorine decomposes water, setting free oxygen ; it is therefore indirectly a strong oxidizing agent. Hydriodic acid, on the other hand, is a strong reducing agent, because of its ready decomposition, thus $2HI + O = H_2O + I_2$.

Hydrobromic acid when dissolved in water to form a weak solution decomposes the water, as chlorine does. When in strong solution, however, it is decomposed by oxygen, as hydriodic acid is.

8.—Questions and Exercises.

1. **Dissolve** some bromine in water, then shake up with this solution some chloroform. Explain the result observed. Would ether or carbon bisulphide answer instead of chloroform?

2. **If** a person wished to make a 2% solution (by weight) of bromine in water, how much bromide of ammonium should he decompose, assuming that he has a liter of water, and that 10% of the bromine set free is lost?

3. How may bromine be separated from water?

4. Some phosphorus is lowered into a jar of chlorine and after chemical action has ceased, some water is added. If you were asked to determine whether you then had a solution of chlorine or of hydrochloric acid, how would you proceed, keeping in mind that the solution also contains an acid of phosphorus? If bromine were substituted for chlorine, in the foregoing question, how should the answer be altered?

5. Dissolve a portion of any bromide and add chlorine water. Divide the liquid into two parts. Boil one portion; to the other add potassic hydrate solution, and afterwards sulphuric acid.

Describe the changes observed, and write equations to explain them.

6. Compare, physically and chemically, bromine with nitrogen tetroxide. How may they be distinguished?

7. Water containing chlorine in solution gradually acquires acid properties. Is the same true of bromine? How may the results be accounted for?

8. Dissolve some potassic bromide, add sulphuric acid slowly as long as the brown colour of the solution is deepened, then shake up with chloroform.

9. Fill out the following schedule, so as to present a comparative view of the relations of the halogens mentioned :—

	CHLORINE.	BROMINE.	IODINE.
(1) Atomic weights			
(2) Physical condition at 20° C.....			
(3) Boiling point..................	—34	—63	200
(4) Melting point		—24	114
(5) Sp. gr. (vapour or gas, air = 1).	2.43	5.54	8.71
(6) Sp. gr. in solid or liquid state .	1.33	3.18(liquid)	4.97 (solid)
(7) Odour			
(8) Colour......................			
(9) Chemical activity.......			
(10) Bleaching			
(11) Hydrogen compounds.........			
(12) Oxy-acids			
(13) Basicity of acids........... .			
(14) Colour of the silver salt of hydrogen acid			
(15) Colour imparted to starch by the element			

10. Place side by side two bottles of solution of chlorine, pass hydrogen sulphide through one for an hour, then test both for acidity.

11. Solution of iodine was added to ammonium hydrate, when the liquid became clear, chlorine was added. Write equations for the reactions. What would have been the effect of adding hydrochloric acid instead of chlorine?

12. Try if iodine in solution will unite directly with iron, zinc and lead. Use filings of the metals.

13. Fill a test-tube with hydriodic acid gas and drop a little strong nitric acid into it.

14. Expose a solution of hydriodic acid to strong light for some time. Repeat, using potassic iodide solution.

15. Pass some chlorine into a vessel filled with hydriodic acid gas. Lower a red hot wire into a vessel of the gas.

16. What would be the result of passing alternately hydrogen iodide gas and oxygen into a jar containing nitrogen tetroxide?

CHAPTER II.

SOME CHEMICAL LAWS AND THEORIES.

1.—Law of Multiple Proportions.

Analyses of the oxides of carbon which led Dalton to the discovery of the law of multiple proportions, gave the following results:

Carbon monoxide. . carbon 42.86, oxygen 57.14
Carbon dioxide. . . . " 27.27, " 72.73

From this it follows that there is relatively twice as much oxygen by weight in the dioxide as in the monoxide, or that in the monoxide 12 parts of carbon, by weight, unite with 16 of oxygen; and in the dioxide, 12 of carbon with 32 of oxygen. Hence one volume of carbon unites with one of oxygen in the monoxide, and with two in the dioxide.

Analyses of marsh gas and olefiant gas give the following percentages :

Marsh gas. . . .carbon 74.95, hydrogen 25.05
Olefiant gas... "   85.68,   "   14.32

Nitrous and nitric oxides yield respectively :

Nitrogen. . . .63.71, oxygen 36.29
and   "   46.75,   "   53.25

Does the same conclusion follow from these figures as from those of the oxides of carbon ?

2.—Isomorphism.

Nearly every chemical salt has a definite form of crystallization, and it is well known that crystals of different systems will not form in combination ; thus if solutions of two salts that crystallize in different forms be mixed and evaporated, the crystals of one salt will be quite distinct from those of the other.   It is known also that if the salts crystallize in the same system and are of similar chemical composition, the two substances will sometimes be found in the same crystal, that is, in crystalline structure, their molecules appear to be interchangeable.   Such substances are said to be **isomorphous.**   Examples are the alums and the alkaline chlorides.   The statement regarding these crystalline interchanges has been formulated as the **law of isomorphism.**   It has been of value as a confirmatory test in determining atomic weights and arriving at conclusions about molecular structure, though there are many excep-

tions to it. This law may be stated as follows: Crystalline structure is dependent only on the number and arrangement of atoms in the molecule, and not at all on their chemical properties. Hence isomorphous substances probably have molecules made up of equal numbers of atoms.

3.—Dulong and Petit's Law.

Early in the present century Dulong and Petit announced, as a result of their investigations, that "the atoms of all simple bodies have the same capacity for heat." While this is not exactly the case, because the same element very generally has different specific heats at different temperatures, it is true within small limits if the specific heat be taken in that range of temperature at which it is about constant.

Now, in a unit weight of oxygen there is one-sixteenth as many atoms as in a unit weight of hydrogen (from Avogadro's law), and since the capacity of each atom for heat, whether oxygen or hydrogen, is the same, it follows that the capacity for heat (specific heat) of a mass of oxygen will be one-sixteenth that of an equal mass of hydrogen, but atomic weight is sixteen times greater, hence the product of specific heat and atomic weight is the same for both. This product for all elements is nearly constant, viz., 6.4.

This principle has been worked out directly by the determination of the specific heats only in the case of solid elements, and indirectly for a few gaseous ones.

The product of specific heat and atomic weight is called **atomic heat.**

The specific heat of 34 solid elements has been directly determined, 28 of these have an atomic heat of 6.4, while 6 vary between that and 5.5.

This law is of value in determining atomic weights.

4.—Some Conditions of Chemical Action.

It is generally true that if solutions of two soluble salts be mixed, and if these salts by metathesis will form an insoluble compound, that compound will be formed. Sodium sulphate and calcium chloride give sodium chloride and calcium sulphate, the latter being nearly insoluble. Calcium sulphate and barium nitrate form calcium nitrate and barium sulphate, the latter quite insoluble.

Again if two salt solutions by their interaction form a compound volatile at ordinary temperature, that compound will likely be produced. The preparation of hydrochloric acid, ammonia and marsh gas furnish examples.

5.—Influence of Mass on Chemical Action.

The particular compounds formed when two substances interact chemically are frequently determined by the relative quantities or masses of the substances present, thus: P_2O_3 or P_2O_5 is formed as the quantity of phosphorus or oxygen is in excess. Antimony and solution of hydrochloric acid in a little water form antimony trichloride $SbCl_3$; but an excess of water throws down the precipitate $SbOCl$, thus :—$SbCl_3 + H_2O = SbOCl + 2HCl$.

Arsenic pentoxide solution through which a rapid current of hydrogen sulphide is passed yields arsenic pentasulphide.

$$As_2O_5 + 5H_2S = As_2S_5 + 5H_2O.$$

If, however, the hydrogen sulphide be passed slowly into the pentoxide solution, the following reaction takes place.

$$As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S.$$

The oxide of carbon formed in combustion is partially determined by the quantity of oxygen as compared with the quantity of carbon available for the chemical action.

6.—Influence of Temperature.

Examples are common enough of change of temperature causing or hindering chemical action. In some cases the compound formed is determined by the temperature to which the constituents were subjected. Barium oxide, BaO, heated to dull redness in oxygen or air becomes barium dioxide, BaO_2; heated a few degrees higher, however, it changes into the monoxide again.

From potassic nitrate and sulphuric acid is obtained either nitric acid, or water and oxides of nitrogen, dependent on whether the temperature is high enough to prevent the constituents of the acid from uniting as they are set free.

Sulphur trioxide at a red heat breaks down into the dioxide and oxygen. Hydrogen and oxygen unite at the temperature of a gas flame to form water, but at $2500°$ it breaks up again into the original gases.

Oxygen and mercury do not combine at ordinary temperatures. When heated they do unite slowly, but at a little higher temperature the compound is broken down into its elements ; so that there is but one narrow range of temperature at which the union is possible. Compare ammonium chloride and potassic chlorate.

7.—Influence of Pressure.

In some cases chemical combination can only be brought about by applying pressure to the mixture of gases that form the union. In many other cases the temperature at which combination takes place is lowered by the application of pressure to the mixture of the constituents. This is a matter of some importance as pointing to chemical action being promoted by other forms of energy than heat.

8.—Catalytic Action.

The influence which a third substance has in promoting chemical action between two others is called catalysis. The effect of manganese dioxide in forming oxygen and potassic chloride is an example. Recent investigations seem to show that this is a very common thing in chemical actions. Commonly carbon monoxide and oxygen explode when mixed and brought into presence of a flame. If both are perfectly dry no union whatever will take place. A very minute trace of water vapour will cause the combination to occur.

CHAPTER III.

1.—Hydrogen.

Hydrogen, in its characteristics, partakes somewhat of the nature of a metal. This statement is based on the following considerations :—

(1) The compounds called acids resemble metallic salts in their composition, so that they may be called hydrogen salts ; and the hydrogen in the molecule of an acid may be replaced by an ordinary metal just as one metal replaces another. A piece of metallic zinc immersed in copper sulphate solution displaces the copper and forms zinc sulphate ; similarly a piece of zinc in lead acetate solution will displace the lead to form zinc acetate ; mercury replaces silver in silver nitrate. In such cases the more electro-positive of the two metals replaces the other one, and as all the metals are electro-positive with regard to hydrogen, they all displace hydrogen from its salts. Metallic salts are crystalline compounds ; hydrogen salts are largely, though not by any means universally, crystallizable.

(2) Metals being in general basic in character, do not form chemical combinations with each other, except in a very few cases. They do form, though, certain mixtures somewhat akin to solutions, called alloys and amalgams. Similar to these are some cases in which hydrogen forms

with a few metals a combination of the nature
of an alloy, in which the hydrogen becomes
solid.   These combinations occur notably with
palladium and platinum.   There are also a few
definite chemical compounds existing as hydrides
of the metals.   The hydrides of sodium, iron and
copper are examples.

(3) Most metals form definite compounds with the
hydroxyl group, OH, so does hydrogen, in the
case of water, H(OH).   The metals of the
sodium group replace the hydrogen atom joined
to the hydroxyl in this compound to form the
alkaline hydrates.

(4) Hydrogen conducts heat and electricity,—dis-
tinctly metallic characters,—and in the solid
form it may be magnetized.

On the other hand, hydrogen seems to occupy a posi-
tion midway between the metals and non-metals, because
(1) its oxides are neither acidic nor basic.   (2) In the
electro chemical series it is at the negative end of the list
of metals, and at the positive end of the non-metals.

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CHAPTER IV.

THE ALKALINE METALS.

1.

They are sodium, potassium, lithium, rubidium, caesium and the hypothetical metal ammonium. Of these, only the first two and ammonium require to be studied here.

Sodium and potassium are both white metals, so soft as to be easily cut, they rapidly oxidize in the air, are readily fusible and burn to white oxides. They both decompose water at ordinary temperatures, forming free hydrogen and the hydroxides of the metals. The oxides and hydroxides are both strongly alkaline, and both are readily soluble. The oxides in solution form hydroxides. Both the oxides and hydrates are strongly basic and never form acids. They are both monads forming compounds of the type MCl, but they form hydrides of the composition M_2H. Each metal combines with its own hydrate, when fused, to yield the oxide and free hydrogen, thus,—$M_2 + 2MHO = 2M_2O + H_2$. The hydrates are not decomposed by heat (compare calcium group), but they are fusible and are very easily soluble in water. The chemical energy of the group increases with the atomic weight.

| METAL.	AT. WEIGHT.	SP. GR.	MELT'G PT.	SP. HEAT
Lithium.....	7	.594	180°	.941 (gas)
Sodium	23	.972	95.6°	.293
Potassium...	39	.865	62.5°	.166
Rubidium ...	85	1.52	38.5°	
Caesium.....	133			

2.—Sodium.

EXPERIMENTS.

1. Hold a loop of platinum wire which has been dipped in a solution of any sodium salt in a non-luminous flame.

2. Try if sodium nitrate gives an alkaline reaction with litmus or forms a precipitate with silver nitrate. Then strongly ignite some of this nitrate either on mica, or in a hard glass tube. Dissolve the remainder and repeat the tests.

$2NaNO_3 = 2NaNO_2 + O_2 = Na_2O_2 + 2NO + O_2$. When taken together, these may be written $2NaNO_3 = Na_2O_2 + 2NO_2$.

3. Drop some bits of sodium on a little water in an evaporating dish; after a strongly alkaline solution has been obtained, neutralize it with hydrochloric acid, then pour the clear liquid into its own bulk of strong ammonia, and lead a current of carbon dioxide into the mixture.

$$Na_2 + 2H_2O = 2NaHO + H_2. \quad NaHO + HCl = NaCl + H_2O$$
$$NaCl + NH_4OH + CO_2 = NaHCO_3 + NH_4Cl.$$
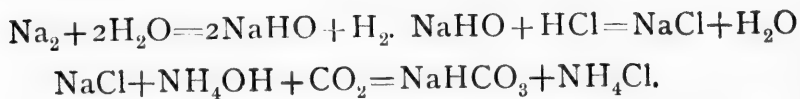
The precipitate is the bicarbonate of sodium (baking soda).

4. Heat some of the bicarbonate of soda strongly and lead the gas that comes off into lime water.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

5. Try if the carbonate can be changed into the oxide by heating, as in the case of calcium. The resulting substance may be tested by dissolving it with water and

trying if it will throw down an insoluble hydroxide of any of the heavy metals such as silver, iron or tin. See that the precipitate is not a carbonate.

6. Dissolve some sodium carbonate and boil it with lime, keeping the whole stirred. After boiling for some time, decant the liquid and test for sodium hydroxide.

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$
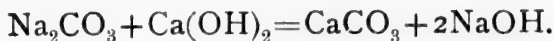
7. If sodium dioxide Na_2O_2 is formed when sodium is burned in air, it should yield hydrogen dioxide with an acid. Try it, by burning a piece of sodium on mica in the tip of a gas flame, then scrape the oxide into a tube and add some dilute hydrochloric acid. Test with iodide of potash and starch paper.

3.—Notes on Sodium.

Occurrence and Preparation.—On account of its ready union with other elements, sodium is not found native. Its chief compounds that are found as minerals are the chloride, carbonate nitrate and sulphate.

Sodium is prepared either by electrolysis of the fused chloride; by heating together sodium carbonate and carbon to a high temperature and collecting the sodium vapour in naphtha,—$Na_2CO_3 + 2C = Na_2 + 3CO$; or by igniting the hydroxide with carbon,—$2NaOH + 2C = 2CO + H_2 + Na_2$.

The carbonate, however, is obtained either as in ex. 3, —*the ammonia process;* or by altering the chloride,— *Leblanc method.* The latter consists of three operations:

(*a*) $2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$ The hydrochloric acid is condensed for other uses.

The sulphate is known technically as *saltcake.*

(*b*) The saltcake is heated strongly with broken coal and limestone. $Na_2SO_4 + 4C = Na_2S + 4CO.$

(*c*) The sulphide acts on the limestone to form sodium carbonate and calcium sulphide.

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The substance now obtained is called *black ash* from the mixture of coal. By dissolving the soluble parts these are obtained separately, and consist of the carbonate with a little mixture of the hydroxide.

4.—Compounds.

Oxides.—Sodium forms two compounds with oxygen, Na_2O, sodium oxide, and Na_2O_2, sodium peroxide or dioxide. The monoxide, Na_2O, is obtained pure by heating sodium with the fused hydroxide. When sodium burns in air a mixture of the monoxide and dioxide is formed, and when the metal is ignited in oxygen or nitrous oxide the dioxide is produced. It may also be prepared as in ex. 2. When either of the oxides is dissolved in water, —and they dissolve very readily,—the hydroxide, $NaOH$, is formed, in the case of the dioxide, oxygen is set free at the same time. The hydroxide is a strongly alkaline monad base. Its ready solubility makes it a valuable reagent.

Chloride.—Sodium chloride, common salt, $NaCl$, is an extensively occurring mineral. It is prepared either by

direct union of the elements or by the action of hydrochloric acid on the oxide, hydroxide or carbonate.

Carbonates.—The bicarbonate, $NaHCO_3$, (baking soda) is the first product obtained. From this the neutral carbonate, Na_2CO_3, (washing soda) is got by heating. Other reactions that are of theoretical interest for the preparation of these salts are (*a*) by passing carbon dioxide into a solution of the hydrate, thus: $2NaHO + CO_2 = Na_2CO_3 + H_2O$; (*b*) by passing CO_2 into a solution of the normal carbonate: $Na_2CO_3 + H_2O + 2CO_2 = 2NaHCO_3$. When the bicarbonate is heated it loses water and carbon dioxide, the exact reverse of the reaction with CO_2. In the acid carbonate, the hydrogen may be replaced by alkalies, thus producing $NaKCO_3$, $NaNH_4CO_3$, etc.

Nitrate.—The nitrate of sodium may be prepared by the action of nitric acid on the oxides or carbonates. It is found in great quantities in the nitrate beds of Peru, and is known as Chili saltpetre.

Sulphur Compounds.—The following sulphides of sodium are known: Na_2S, Na_2S_2, Na_2S_4, Na_2S_5. They are of interest chiefly because of their resemblance in composition to the oxides. When the metal is heated with sulphur, a mixture of sulphides is formed. Hydrogen or carbon heated with the sulphate reduces it thus:—

$$Na_2SO_4 + 4H_2 = Na_2S + 4H_2O$$
$$Na_2SO_4 + 4C = Na_2S + 4CO.$$
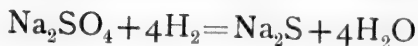
When sodium chloride is fused in hydrogen sulphide, the following reaction occurs:—

$$H_2S + 2NaCl = Na_2S + 2HCl.$$

Sulphuretted hydrogen forms with the hydroxide a hydro-sulphide, $NaOH + H_2S = NaHS + H_2O$. This compound can also be obtained by the action of sodium on hydrogen sulphide, $Na_2 + 2H_2S = 2NaHS + H_2$ (compare sodium on water). With sulphuric acid, the oxide or carbonate forms a *sulphate*, Na_2SO_4 (Glauber's salt). It is also produced extensively in the manufacture of soda ash, by Leblanc's process, when the chloride is treated with sulphuric acid.

The *thiosulphate*, commonly called hyposulphite, $Na_2S_2O_3$. This is the sodium salt of thio-sulphuric acid, $H_2S_2O_3$. If sulphur dioxide be passed into a solution of caustic soda, sodium sulphite Na_2SO_3 is formed, and when this is boiled with sulphur, the thiosulphate is produced.

Hydrides.—When sodium is heated in a current of hydrogen the hydride Na_2H is produced. It is decomposed readily by heat, and, in presence of mercury, breaks up to form an amalgam of sodium and free hydrogen.

The very strong basic properties of sodium oxide almost make the number of the salts into which it enters to be limited only by the number of acids known.

5.—Tests.

(*a*) The yellow colouration of the flame.

(*b*) Sodium salts, when acidified with hydrochloric acid, form red crystals with platinic chloride.

6.—**Potassium.**

This metal resembles sodium very much. The experiments with sodium may be repeated, but in each case the corresponding potassium compound is to be substituted for the sodium one. The flames of potassium and sodium should be compared, when looked at through a piece of blue glass. This cuts off the yellow sodium rays.

7.—**Notes on Potassium.**

Occurrence and Preparation.—Potassium is a constituent of wood ashes, in which it exists mostly as a carbonate. It is also one of the substances contained in felspar; and from the disintegration of felspathic rocks it becomes an ingredient of clay. It occurs as a chloride forming the mineral *sylvite*, and as the nitrate it forms an incrustation on dry soils in some parts of the world. The metal is prepared just as sodium is.

8.—**Compounds.**

The hydride, K_2H, the monoxide, K_2O and dioxide, K_2O_2, the hydroxide, KOH, the nitrate, KNO_3, chloride, KCl, and sulphate, K_2SO_4, are prepared in ways similar to those employed for the corresponding sodium compounds.

Oxides.—Four oxides of potassium are known. They are monoxide, K_2O, formed (along with the dioxide) when the metal is burned in air, or when the metal is fused with the hydrate; dioxide, K_2O_2, produced by com-

bustion in air, or in oxygen, in the former case it is mixed with monoxide, in the latter, with trioxide K_2O_3, and tetroxide K_2O_4. These higher oxides, with the hydroxide, are also produced by the decomposition of K_2O_2 in air in presence of water vapour. A possible reaction is indicated thus :—

$$3K_2O_2 + H_2O + O_2 = K_2O_3 + K_2O_4 + 2KHO.$$

All the other oxides are reduced to K_2O at high temperatures.

Iodide.—This important compound, KI, is obtained mixed with the iodate KIO_3, when iodine is introduced into the hydrate and heated. (Compare High School Chemistry, p. 170.)

$$6I + 6KOH = 5KI + KIO_3 + 3H_2O.$$

The iodide is soluble in alcohol, but the iodate is not, hence they can be separated. The iodide may also be prepared by the direct action of the elements, or by acting on the hydroxide, oxide or carbonate of the metal with hydriodic acid.

Iodate, KIO_3, and periodate, KIO_4, are two other potassic compounds of iodine.

Chlorine Compounds.—The most important of these are the *chloride* and *chlorate*. The former is prepared in ways similar to those in which the iodide is obtained, or by decomposing the chlorate by heat.

The chlorate has been partly described in High School Chemistry, page 170. It is valuable chiefly as an oxidizing agent, and as a source of oxygen.

Potassic hypochlorite, KClO, results from the action of chlorine upon caustic potash, $2KOH + Cl_2 = KClO + KCl + H_2O$.

On boiling the mixture the hypochlorite breaks up into the chloride and chlorate, $3KClO = KClO_3 + 2KCl$.

Sulphur Compounds.—The monosulphide, K_2S, may be prepared by fusing the sulphate with carbon, $2C + K_2SO_4 = K_2S + 2CO_2$.

The polysulphides K_2S_2, K_2S_3, K_2S_4 and K_2S_5 are all obtained by boiling the monosulphide with sulphur.

A hydrosulphide, KHS, is formed when caustic potash solution is saturated with hydrogen sulphide. It is probable that the monosulphide is converted into the hydrosulphide and hydroxide by the action of water, thus :—$K_2S + H_2O = KHS + KHO$. This is analogous to the reaction of the oxide with water. The polysulphides, in presence of acids, break down into hydrogen suphide and sulphur.

$$K_2S_3 + 2HCl = H_2S + 2KCl + 2S.$$

Other Compounds.—Potassium unites with the cyanogen radical to form potassium cyanide, KCN. This is obtained from the decomposition of ferrocyanide of potash by heat.

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

If an oxidizing substance or sulphur be present, the cyanate, KCNO, in the former case, or the sulphocyanide, KCNS, in the latter case is formed.

9.—Tests.

(*a*) The flame colour of pale violet or lilac, but appearing red through blue glass or indigo solution.

(*b*) With tartaric acid, $H_2C_2H_4O_6$, or with its acid sodium salt, potassium forms a white granular crystalline precipitate.

(*c*) With platinic chloride, $PtCl_4$, potassium salts, in solution, form a yellow precipitate, but often it is necessary to stir the mixture for some time.

10.—Ammonium.

The hypothetical metal NH_4 belongs to the group of the alkalies. Its supposed amalgam with mercury has been referred to in High School Chemistry, page 109. When the amalgam is cooled below freezing point it forms a brittle metallic mass. The chief ground, however, for believing that there is a metal having the molecular composition NH_4 is the resemblance of its salts in number and character to those of the alkaline metals, particularly potassium. The following is a partial list of compounds of potassium and ammonium, not by any means complete, but sufficient to show the marked similarity. Each unites with the groups: HO, S, S_2, S_3, S_4, S_5, SO_3, HSO_3, SO_4, HSO_4, NO_3, NO_2, Cl, Br, I, CN, SCN, $Al(SO_4)_2$, CO_3, HCO_3, AsO_4, AsS_4. It will be observed that these are precipitation compounds, or else those formed by double displacements by heating. The compounds of ammonium corresponding to those of potassium obtained by heating the metal are

not formed because the ammonium hydroxide breaks down into ammonia and water. Another difference is that when the ammonium halides are heated they break up into ammonia and the corresponding halogen compound of hydrogen. This is not the case with the other alkalies.

Ammonium salts are isomorphous with those of potassium (see page 12).

Ammonium salts, when heated, are decomposed; thus the chloride breaks up into ammonia and the acid, but on cooling these again unite. Sodium or potassium hydrate displaces ammonium hydrate from its compounds and sets ammonia free.

11.—Tests.

(*a*) Pungent odour and effect on litmus and turmeric.

(*b*) Solution of an ammonium salt boiled with a caustic alkali sets free ammonia.

(*c*) Nessler's test solution.

12.—Questions and Exercises.

1. Potassium and sodium may be obtained by igniting some of their compounds with carbon or hydrogen. Why can not the ammonium radical be got in a similar way?

2. "The acid character of hydrogen sulphide and its basicity would lead one to expect that with caustic alkalies two replacements

would be possible, resulting finally in M_2S where M is the metal of the alkali." Explain this statement. Does the actual result correspond with the theoretical?

3. Boil some solution of sodium hydrate in a test-tube with a little powdered sulphur, after it has become dark coloured add a few drops of hydrochloric acid. Smell the escaping gas. Write equations for the reactions.

4. Sodium hydrate is heated with sodium, some dilute nitric acid is added, the result evaporated to dryness and ignited ; the residue treated with a solution of sulphur dioxide, again evaporated and ignited with carbon in the air. Trace the chemical changes, with equations.

5. (*a*) Steam is passed through a tube containing some pieces of sodium. (*b*) Hydrogen is passed over heated sodium oxide. Is there a chemical action in either case? In both?

CHAPTER V.

METALS OF THE CALCIUM GROUP (ALKALINE EARTHS): CALCIUM—STRONTIUM—BARIUM.

1.—Group Characteristics.

All are yellowish metals, obtained by electrolysis of the fused chlorides. They form oxides of the composition MO, peroxides, MO_2, hydrates, $M(HO)_2$, which are sparingly soluble forming weak alkaline solutions.

The hydrates, when strongly heated, are decomposed into the oxide and water, thus $M(HO)_2 = MO + H_2O$.

The carbonates are decomposed by heat into the oxides and carbon dioxide, $MCO_3 = MO + CO_2$.

The oxides are strongly basic, that of calcium being the weakest and of barium the strongest; thus chemical energy increases with atomic weight.

The carbonates, phosphates and sulphates are almost, or entirely, insoluble.

2.—Calcium.

EXPERIMENTS.

1. Bend the end of a bit of platinum wire into a loop, with this hold a little of some calcium salt in the non-luminous flame of a Bunsen burner.

2. Powder a piece of marble, and try if it is soluble in water. Drop some of the powder into some hydrochloric acid diluted one-half with water. When gas ceases to come off, evaporate a part of the liquid to dryness, and keep the powder obtained. To a second portion of the liquid add some dilute sulphuric acid, and filter. To another portion add excess of sodium carbonate solution, and filter. The salts obtained are calcic chloride, calcic sulphate and calcic carbonate. Write equations for the entire reactions.

3. Try if the sulphate is at all soluble. To do this shake it up with a large quantity of water, and let it stand for some time, then test the clear fluid with barium nitrate solution.

4. Test a little of the solution of the chloride with a solution (not too dilute), of any soluble sulphate to see

if there is calcic sulphate formed.   What reason is there for the direction "not too dilute"?

5. Heat strongly some of the carbonate in a small crucible for some time.   Test with moist red litmus paper.   Does the unheated carbonate give a similar result?   Try if a piece of marble, a piece of chalk (not common crayon), and a bit of oyster shell will act as the carbonate does. $CaCO_3$ when heated is decomposed into CaO and CO_2.   CaO is lime ; try if it will dissolve in water.   To do this shake it up with water and after the sediment has settled test the liquid with red litmus paper.

6. Pour into a solution of chloride of calcium a little solution of sodium phosphate.

7. Repeat the last experiment, but use an alkaline oxalate instead of the phosphate. $CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl$.   Examine the crystals when they form.

8. Will other soluble carbonates act like that of sodium in ex. 2?

9. Let some lime water (solution of calcic oxide) stand in an open vessel exposed to the air of a schoolroom for a couple of days, then pour out the liquid, leaving the white scum on the side of the vessel.   Drop a little dilute acid on this scum.   What is it?   Has the alkalinity of the liquid been affected?

10. Place a bit of slaked lime in a test-tube and heat it strongly.   Water should be formed on the cold part of the tube.

3.—**Notes on Calcium.**

Occurrence.—Calcium never occurs free, but in combination it exists in vast quantities as limestones, chalk, gypsum, marble and apatite.

Calcium and Oxygen.—Calcic oxide, CaO, quicklime, is formed by igniting the carbonate in presence of air. $CaCO_3 = CaO + CO_2$. If the carbon dioxide be allowed to surround the carbonate, decomposition does not occur. With water it forms the hydrate $Ca(OH)_2$, slaked lime, which is slightly soluble, the solution being *lime water*. The undissolved hydroxide suspended in water is *milk of lime*.

Mortar is a mixture of calcic hydroxide and sand with water ; the hardening of it is due to the hydrate absorbing carbon dioxide from the air to form the carbonate, and at the same time acting on the sand to produce a silicate of calcium.

Calcium forms a second oxide, CaO_2, by the action of calcic hydrate solution on hydrogen dioxide. It is a true peroxide, that is, loses oxygen when acted on by acids, because it is then reduced to the basic oxide CaO. The peroxide is a hydrated compound, its full formula being $CaO_2 + 8H_2O$.

Calcium and the Halogens.—The most important of these is calcic chloride $CaCl_2$. It is prepared by acting on calcic carbonate with hydrochloric acid, or, when chlorine is passed into cold dry slaked lime, a mixture of the chloride and the hypochlorite is formed, this is *bleaching powder* This substance is commonly supposed to be $CaCl_2 + Ca(ClO)_2$, but there is reason for believing

it to be CaCl(OCl). See H. S. Chem., p. 169. Calcium fluoride (fluor spar), CaF_2 is an insoluble mineral, the source of fluorine. (Compare potassium.)

Calcium Carbonate.—This occurs in nature in many forms; some of the most important are chalk, limestone, marble, calc spar, arragonite, dolomite, coral rocks and shells of animals. It may be prepared by treating any soluble calcium salt with a solution of a carbonate. When heated it yields the oxide and carbon dioxide. It is insoluble in water, but soluble, to some extent, in solution of carbon dioxide, probably forming $Ca(HCO_3)_2$. See H. S. Chem., p. 129.

Other Compounds.

Calcium Chlorate, $Ca(ClO_3)_2$ formed by passing chlorine into a hot solution of the hydrate. See H. S. Chem., pp. 161, 170.

Calcic Sulphate, gypsum, $CaSO_4$ is found in nature. When heated to $110° - 140°$ and powdered it forms plaster of Paris, which readily absorbs water and hardens (*sets*).

Calcic Phosphate, $Ca_3(PO_4)_2$ is the chief ingredient of apatite (*phosphates*), and is the mineral constituent of bones. This has already been referred to under the preparation of phosphorus.

Calcium Sulphide, CaS is obtained by heating the sulphate with powdered charcoal, $CaSO_4 + 2C = CaS + 2CO_2$.

4.—Strontium.

EXPERIMENTS.

1. Hold a bit of strontium nitrate on a platinum loop in a non-luminous flame.

2. Drop a little solution of calcic sulphate into a solution of nitrate of strontium. If necessary let this stand for some time until a white precipitate appears ; filter and dry the precipitate. By the flame test determine whether it is a calcium or strontium salt.

3. Try to repeat this experiment, but use instead of calcic sulphate solution, water in which barium sulphate has been shaken, and has become clear by settling.

4. Mix a little solid nitrate of calcium and nitrate of strontium. Try to dissolve the mixture in absolute alcohol. After shaking for some time, filter, evaporate the filtrate and test in the flame both the part dissolved and that left.

5.—Notes on Strontium.

Strontium is found in nature chiefly as two minerals, strontianite and celestine, the carbonate and sulphate, respectively, of strontium.

Compounds.—Strontium resembles calcium very much, but chemically it occupies a place between calcium and barium. The two oxides SrO and SrO_2, and the hydroxide are prepared in the same manner as the corresponding calcium compounds. The sulphate $SrSO_4$, the nitrate $Sr(NO_3)_2$, and the chloride, $SrCl_2$, are obtained by treating the carbonate $SrCO_3$ with the proper acids.

6.—Barium.

EXPERIMENTS.

1. Treat a little of any barium salt with strong hydrochloric acid, then ignite it on a platinum loop

2. To a solution* of barium nitrate, add a solution of ammonium carbonate, filter the precipitate, dry it. Try if it is a barium salt, by the flame test. Test it also with a few drops of strong acid for a carbonate.

3. Heat some barium carbonate as calcium carbonate was heated to drive off the carbon dioxide. Try with strong acid if the carbonate has been decomposed. If it was not, raise it to a high temperature (this will require a b. . . . mp flame) for some time. This should at least partly decompose the salt into BaO and CO_2.

4. Try if the white solid left from the last experiment is at all soluble in water. This may be done by testing the liquid with litmus and with a drop of dilute sulphuric acid.

5. Heat a small quantity of barium nitrate in a crucible. After all effervescence has ceased test the residue for barium oxide by treating with water and using litmus or turmeric. This really tests for the hydroxide $Ba(OH)_2$, which is formed in the same way that $Ca(OH)_2$ is.

6. Dissolve some of a barium salt, say the chloride, in dilute hydrochloric acid. Divide the solution into two, parts. Add to one part strong nitric acid, to the other strong hydrochloric acid until a precipitate forms. (The fact that a precipitate does form with strong hydrochloric acid should be kept in mind else errors will occur in systematic testing and barium will be mistaken for one of the elements whose chlorides are insoluble.) After a distinct precipitate has formed add water. Is the chloride soluble?

Note.—Barium salts that are not readily soluble in water may be dissolved in weak hydrochloric acid.

7. Mix solutions of any barium salt and bichromate of potash $K_2Cr_2O_7$. Repeat, but use instead of barium a solution of a strontium, then of a calcium salt.


7.—Notes on Barium.

Occurrence.—Barium is chiefly found in the form of two of its insoluble salts, the carbonate $BaCO_3$, (witherite) and the sulphate $BaSO_4$ (heavyspar).

Compounds.—The combinations of barium are very similar to those of calcium, except that they are more stable.

The *oxide*, when heated in oxygen or air to dull redness, becomes the dioxide ; and when heated still higher changes again to the monoxide yielding free oxygen. This method has been used for the preparation of oxygen. When barium oxide is brought into contact with water, barium hydroxide $Ba(OH)_2$, is formed ; and this, when dissolved in water, yields an alkaline solution, baryta water, similar to lime water. Baryta water is affected by carbon dioxide just as lime water is.

Barium carbonate is much more difficult of decomposition by heat than is calcium carbonate ; indeed it is hardly possible to drive off all the carbon dioxide. In this particular the carbonate has some resemblance to those of the alkaline metals, which are not at all broken up by heating.

Barium sulphide is prepared by passing hydrogen sulphide into barium hydrate.

$$Ba(OH)_2 + H_2S = BaS + 2H_2O.$$
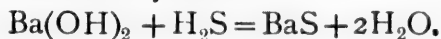
Barium sulphide with water forms the hydroxide and hydrosulphide of barium, thus :— $2BaS + 2H_2O = Ba(OH)_2 + Ba(HS)_2$.   (Compare alkaline metals.)

8.—Tests for the Calcium Group.

(1) Alkaline carbonates, such as $(NH_4)_2CO_3$, give a white precipitate in neutral or alkaline solutions of the salts.

(2) A soluble sulphate throws down a white precipitate.

(3) A solution of calcic sulphate yields a white precipitate with salts of Sr and Ba.

(4) Alkaline oxalates give white precipitates in presence of ammonia. Acetic acid, $HC_2H_3O_2$, dissolves barium and strontium oxalates slightly, but that of calcium scarcely at all.

(5) Sodium phosphate yields a white precipitate with each metal in presence of ammonia.

The elements of the group are distinguished from each other

(a) By the flame test.

(b) By solution of $CaSO_4$ forming precipitate with Sr and Ba.

(c) By bichromate solution, see ex. 7.

9.—Questions and Exercises.

1. If bleaching powder, in solution, were boiled, chlorine would be set free, what would be the effect of this on the other components of the mixture ?

2. What compound is left when eggshells are burned?

3. Drop a lump of calcic carbonate into sulphuric acid. What happens, and why?

4. (*a*) Dissolve a little lead acetate; decant the clear solution, then drop into it some hydrochloric acid. (*b*) Drop a little saturated solution of barium nitrate into hydrochloric acid. (*c*) Pour gradually strong hydrochloric acid into a little of the saturated solution of a barium salt. These experiments show that in testing with hydrochloric acid there is danger of mistaking barium for lead. How may this be avoided?

5. Make, separately, solutions of barium, strontium and calcium sulphate, add some ammonium hydrate to each, then some solution of ammonium carbonate. After standing, filter and drop a little nitric acid on the powder on the filter paper. Does this give a method of distinguishing between the elements? If the three sulphates had been mixed would this enable you to make any separation? To the filtrate add calcic sulphate solution and let it stand for some time. What now is precipitated? Does this aid in separating the substances?

6. Make solutions of the chlorides of the metals, add strong alcohol (absolute alcohol is much the best) to each. Observe their solubilities. Add a large volume of water to the ones that have dissolved.

7. Compare the metals of the calcium group and of the potassium group in regard to the following:—(*a*) their chemical action with water; (*b*) the effect of heat upon their hydrates; (*c*) the effect of heat upon their carbonates; (*d*) the solubility of their sulphates; (*e*) their distinctive flame colours.

CHAPTER VI.

THE MAGNESIUM GROUP.

The metals of this group are beryllium, magnesium, zinc and cadmium.


1.—Group Characteristics.

All are white metals, not oxidized by exposure to the air. Magnesium and zinc are both oxidized when heated in air, they will both decompose water at high temperatures, both form basic oxides, that of magnesium slightly alkaline, both unite with the halogens. They form one insoluble (nearly, in the case of magnesium) oxide of the composition MO. The carbonates are insoluble.

2.—Magnesium.

EXPERIMENTS.

1. Burn some magnesium under a bell-jar, collect the white powder, try to dissolve it, and test the liquid for alkalinity.

$$MgO + H_2O = Mg(HO)_2.$$
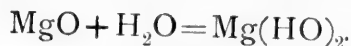
2. Pass steam through a hard glass tube in which is a piece of magnesium wire, heat the tube under the wire and collect the gas that comes off while the metal is burning. Test this gas. Compare the substance in the tube with that obtained in the last experiment.

3. Add to a solution of magnesic sulphate (Epsom salts) some caustic soda, or caustic potash solution.

Add to this, after the precipitate is formed, ammonium hydrate.

Try if ammonium hydrate may be substituted for that of potassium or sodium in the first operation. Add it slowly at first, then in excess. Will solutions of the ammonium salts cause the precipitate to dissolve? Try the chloride, nitrate and sulphate.

4. Add to a solution of magnesic sulphate, a solution of potassic or sodic carbonate, until the mixture ceases to give off gas.

$$2MgSO_4 + 2K_2CO_3 + H_2O = MgCO_3Mg(HO)_2 +$$
$$2K_2SO_4 + CO_2$$
$$= Mg_2(CO_3)(HO)_2, \text{ etc.}$$
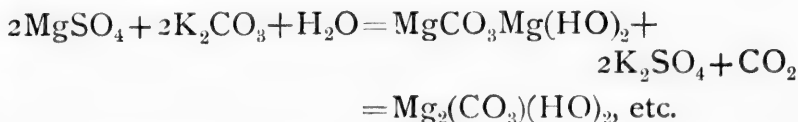
The precipitate is basic carbonate of magnesium. This salt is quite variable in its composition, depending apparently on mass and temperature of the substances used, thus :—

$$3MgSO_4 + 3K_2CO_3 + H_2O = MgCO_3MgOMg(OH)_2 +$$
$$3K_2SO_4 + 2CO_2$$
$$= Mg_3(CO_3)(HO)_2(O), \text{ etc.,}$$
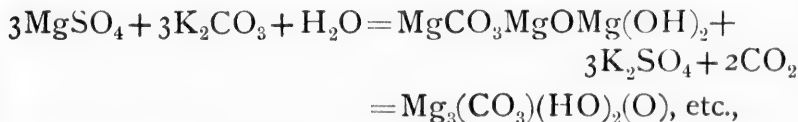
is another form of the reaction. This basic carbonate is usually spoken of as carbonate simply. Pass a current of carbon dioxide into the original solution.

5. If the carbonate be strongly heated it will give off carbon dioxide, as may be shown by its ceasing to effervesce with acids.

6. Treat some magnesic carbonate with hydrochloric acid, evaporate to dryness, then heat.

$$MgCO_3 + 2HCl = MgCl_2 + H_2CO_3.$$

The chloride contains 6 molecules of water and is therefore a hydrated compound. When heated to drive off the water the chloride is decomposed and forms the oxide, MgO.

$$MgCl_2 + 6H_2O = MgO + 2HCl + 5H_2O.$$

7. Treat some solution of a magnesium salt with disodic phosphate. An acid phosphate of magnesium, $MgHPO_4$, is formed. Is it soluble in ammonia?

3.—Notes on Magnesium.

Occurrence.—Magnesium is found as a neutral carbonate, magnesite, $MgCO_3$; as the sulphate, Epsom salts, $MgSO_4$; as a double carbonate with calcium in dolomite; as silicates in serpentine, asbestos, talc, soapstone; and as a chloride, sometimes associated with those of sodium and potassium.

Preparation.—Magnesium is obtained in the metallic state by heating the chloride with sodium. The sodium unites with the chlorine and the magnesium is set free.

Other Properties.—Magnesium is nearly related to the metals of the calcium group, as is shown by the formation of similar oxides and hydroxides which are slightly soluble and slightly alkaline, by the decomposition of the carbonate by heating, by the chlorides crystallizing with the same number of molecules of water.

Magnesium unites with the alkaline metals to form double salts, such as $MgCl_2KCl$ or $MgKCl_3$, $NH_4ClMgCl_2$, $MgSO_4K_2SO_4$, etc. It decomposes water at about $100°$ C., though somewhat slowly.
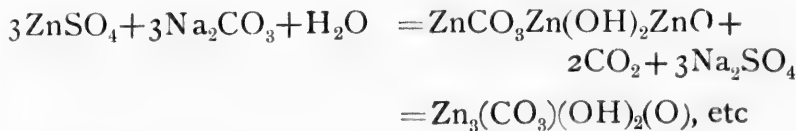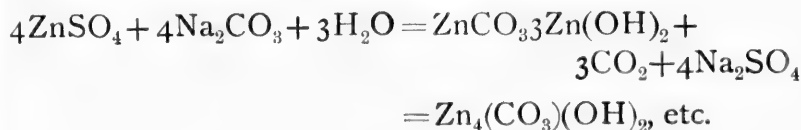
4.—Zinc.

EXPERIMENTS.

1. Heat a cutting of zinc on charcoal in the oxidizing flame. Observe the colour of the oxide when hot, and when cold.

2. Cut a strip of zinc to a point at one end ; hold this end in a gas flame until it melts, continue holding it in the edge of the flame but without letting the melted part drop off. Observe the colour of the flame produced, and the appearance of the zinc oxide formed. Try if a bit of zinc clipping when heated on mica will oxidize and burn in a similar way.

3. Pour on some granulated zinc, separately, some hydrochloric acid, nitric acid, sulphuric acid, diluted in each case. Evaporate the fluid to dryness, wash the salts, dry again and test for a chloride, a sulphate and a nitrate.

4. Make a solution of zinc sulphate and add sodium carbonate. Basic carbonate of zinc is formed, the composition depending largely on accompanying conditions, high temperature and excess of water increasing the basicity. Probably two of these carbonates are formed as follows :—

$$4ZnSO_4 + 4Na_2CO_3 + 3H_2O = ZnCO_3 3Zn(OH)_2 +$$
$$3CO_2 + 4Na_2SO_4$$

$$= Zn_4(CO_3)(OH)_6, \text{ etc.}$$

$$3ZnSO_4 + 3Na_2CO_3 + H_2O = ZnCO_3 Zn(OH)_2 ZnO +$$
$$2CO_2 + 3Na_2SO_4$$

$$= Zn_3(CO_3)(OH)_2(O), \text{ etc}$$

Compare corresponding salts of magnesium.

5. Filter out some of the precipitate of the last experiment, heat it strongly on mica or in a hard glass tube. After it turns yellow, try if it effervesces with an acid

$$ZnCO_3 = ZnO + CO_2, \text{ when h\_\_\_.d.}$$

6. Mix some zinc oxide with powdered charcoal and heat it on charcoal in the reducing flame. This should give metallic zinc.

7. Try if zinc oxide is soluble. Is it alkaline? Use both turmeric and litmus in testing it.

8. Make a solution of zinc sulphate, divide it into three parts. Add to one of these very gradually a solution of sodium hydrate until it is largely in excess. Do the same with the other parts, but use for e potassium hydrate and for the other ammonium hydrate. The precipitate formed at first, in each case, was zinc hydrate $Zn(OH)_2$, thus :—$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$. When the precipitate dissolves, probably the following reaction occurs :

$$Zn(OH)_2 + 2Na(OH) = Na_2ZnO_2 + 2H_2O.$$
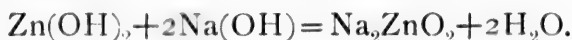
Na_2ZnO_2, called zincate of sodium, has the composition of the sodium salt of an acid H_2ZnO_2.

9. Filter out some of the hydrate of zinc and heat it strongly. It changes to the oxide. $Zn(OH)_2 = ZnO + H_2O$. Compare the similar operations in the cases of the calcium group and of magnesium.

10. Try if a precipitate is formed in a solution of a zinc salt by hydrogen sulphide or ammonium sulphide ; make the former test in both acid and alkaline solutions. After adding the sulphuretted hydrogen, pour in gradu-

ally ammonium hydrate. The white precipitate is zinc sulphide and is the *only white* sulphide of a metal known. Test it for solubility in nitric, hydrochloric, sulphuric and acetic acids.

11. Will hydrogen sulphide precipitate zinc sulphide in presence of excess of potassic hydroxide?

5.—Notes on Zinc.

Occurrence.—The chief sources of the metal are the carbonate, $ZnCO_3$ (calamine), and the sulphide, ZnS (blende). From these, metallic zinc is obtained by converting the ore into the oxide and heating it in closed retorts with charcoal. The metal distils out and collects in cold tubes.

Properties.—Zinc is a white metal, rather brittle at ordinary temperatures, but malleable and ductile at 150°—200°, above 200° it becomes very brittle. It melts at about 430°, boils at about 1000°, hence may be distilled. Zinc burns with a bright somewhat greenish flame. Like magnesium, zinc forms with the alkalies double salts, such as $ZnCl_2 2KCl$, $ZnCl_2 2NaCl$, etc. The zincate of potash, K_2ZnO_2, of ex. 8, may be compared in constitution to this double salt if the chlorine is exchanged for oxygen. This compound corresponds (*a*) to the salt of an acid having the composition H_2ZnO_2, (*b*) to a double salt of zinc and the alkali in which the acid radical, or the halogen is replaced by oxygen, (*c*) to the hydroxide of zinc in which the hydrogen is replaced by the alkaline metal.

Vapour Density.—Vapour of zinc has a density equal to one half its atomic weight, hence *the molecule of zinc must be monatomic.*

6.—Tests for Metals of the Magnesium Group.

For Magnesium.

1. Ammonium hydrate added to a solution of a magnesium salt throws down a white precipitate soluble in ammonium chloride.

2. Hydrogen sulphide gives no precipitate.

3. Phosphate of soda gives a white precipitate.

4. Calcic hydrate solution gives white precipitate.

For Zinc.

1. Ammonium hydrate throws down a white precipitate, which is gelatinous and soluble in excess of the alkali. Potassium and sodium act similarly.

2. Hydrogen sulphide in neutral or alkaline solutions, throws down a white precipitate, soluble in the strong acids.

7.—Questions and Exercises.

1. Try if the result is the same in the following cases :—

   (*a*) A zinc salt in neutral solution is treated with hydrogen sulphide and acetic acid is added (ex. 10).

   (*b*) The solution of the zinc salt is mixed with solution of sodium acetate before the hydrogen sulphide is added.

   (*c*) The sodium acetate is added after the sulphuretted hydrogen.

2. Mix strong solutions of zinc sulphate and calcic chloride. Filter and wash. Test the solid for calcium, and the fluid for zinc. Which contains the sulphate, and which the chloride?

3. Will lime water yield a precipitate with the oxide of magnesium? What would that precipitate consist of?

4. Alkaline carbonates yield what salts with zinc and magnesium? Are both these salts soluble in ammonium chloride solution?

5. In the reduction of zinc ores what is the object of the roasting? What of the heating with charcoal?

6. Heat some zinc sulphate in a hard test-tube until water of crystallization is driven off. Zinc sulphate $ZnSO_4 + 7H_2O$ is isomorphous with magnesic sulphate $MgSO_4 + 7H_2O$. How can they be distinguished most readily?

7. Mix solutions of calcic hydrate and magnesic sulphate. Write equations for the reaction. How could the substances formed be separated?

8. Explain the reactions symbolized by the following equations:

$$MgCO_3 + H_2S + H_2O = MgS + CO_2 + 2H_2O = CO_2 +$$
$$Mg(OH)_2 + H_2S.$$
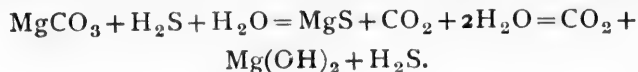
CHAPTER VII.

BORON AND ALUMINIUM.

1.—General Characteristics.

Boron, as isolated, is an amorphous brownish non-metallic powder; aluminium is a silvery white metal. Boron, in this form at least, is a non-conductor of electricity and is infusible, while aluminium is fusible and is a good conductor. It is in their compounds that these substances most resemble each other. They both burn

in air, to M_2O_3. Both decompose water at or above 100°, also forming M_2O_3 and hydrogen. Boron is oxidized by heating with the strong acids, and unites with the halogens, sulphur and nitrogen. The oxide B_2O_3 is acidic, the hydroxide $B(OH)_3$ being known as boric acid. The hydrate of aluminium $Al(OH)_3$ is also feebly acidic with strong bases, but is basic with strong acids, hence basic properties increase with .tomic weight, in the group. Both boron and aluminium are soluble in hot concentrated alkalies with evolution of hydrogen, thus :—

$$2B + 6NaHO = 2B(NaO)_3 + 3H_2.$$
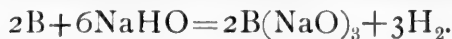
$B(NaO)_3$ is borate of sodium, compare aluminates, page 52.

2.—Boron.

EXPERIMENTS.

1. Dissolve some borax, $Na_2B_4O_7$. Pour off some of the saturated solution and add about one-twelfth of its bulk of sulphuric acid. Heat the mixture to boiling, then allow it to cool. Crystals should form which may be filtered out; these are boric acid $H_3BO_3 = B(OH)_3$.

2. Dissolve some of these crystals in alcohol in an evaporating dish, then set fire to the alcohol. Notice the colour of the flame.

3. Test the solution with turmeric paper, after drying, the paper should be brownish red. Moisten this with ammonium hydrate. Try if acids change the brown produced in the turmeric by boric acid.

4. Heat some of the crystals of boric acid on platinum sheet. Water is driven off and boric oxide B_2O_3 is left as a glassy solid.
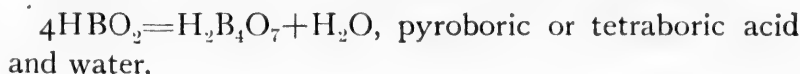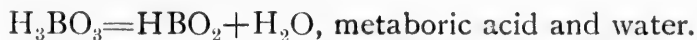
3.—Notes on Boron.

Occurrence.—Borax and boric acids are found as minerals, the latter largely in Italy, the former in Central Asia and California.

Besides in the form of the amorphous powder, boron has been obtained as a crystalline substance, yellowish in colour and transparent. This is done by melting the brown powder with aluminium, then dissolving out the latter substance with acid.

The amorphous form is prepared by heating in a closed iron retort boric acid and sodium with sodium chloride. The molten mass thrown into dilute hydrochloric acid leaves the boron undissolved.

The most important salt of boron is borax, or tetraborate of sodium $Na_2B_4O_7 = Na_2O(B_2O_3)_2$. This is derived as follows:—boric acid is $B(OH)_3$, which, when heated loses water thus,—

$H_3BO_3 = HBO_2 + H_2O$, metaboric acid and water.

$4HBO_2 = H_2B_4O_7 + H_2O$, pyroboric or tetraboric acid and water.

Borax is the sodium salt of this acid.

Borax dissolves many metallic oxides readily, hence its value to metal workers as a flux (solvent for the oxides) that clean surfaces may be obtained for welding and soldering.

Like the other non-metals, boron forms a compound with hydrogen which has the formula BH_3. It also burns readily in oxygen; and, with nitrogen forms a nitride BN_3. With the halogens boron forms compounds of which BCl_3 is a type.

4

4.—Aluminium.

EXPERIMENTS.

1. Examine some metallic aluminium. Do the common acids attack it? Does it oxidize when heated on charcoal in the oxidizing flame?

2. Heat some alum on mica, or in a test-tube,

$$Al_2K_24SO_4 + 24H_2O = Al_2(SO_4)_3K_2SO_4 + 24H_2O.$$

3. Dissolve what remains in ex. 2 and divide the solution into four parts. Drop into one of these solutions, gradually, some ammonium hydrate; into a second, some potassic hydrate solution; into a third, some sodic hydrate solution; and into the fourth some lime water. The precipitate is aluminium hydrate, $Al_2(OH)_6$. Is it soluble in excess of the reagent in any case?

4. Are similar precipitates formed with the unfused alum?

5. Heat some of the hydrate of ex. 3 to redness on mica, the resultant substance is the trioxide Al_2O_3, *alumina.*

6. Moisten a little alumina with solution of nitrate of cobalt and heat to redness.

7. To a solution of alum add an alkaline carbonate,

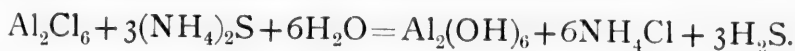$$Al_2(SO_4)_3K_2SO_4 + 3K_2CO_3 + 3H_2O = Al_2(OH)_6 +$$
$$4K_2SO_4 + 3CO_2.$$

Also with the chloride,

$$Al_2Cl_6 + 3K_2CO_3 + 3H_2O = Al_2(OH)_6 + 6KCl + 3CO_2.$$
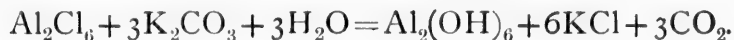
8. Treat a solution of an aluminium salt with hydrogen sulphide. Repeat, using ammonium sulphide. The

precipitate is not the sulphide, but the hydrate formed by the decomposition of the alkaline sulphide.

$$Al_2Cl_6 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 6NH_4Cl + 3H_2S.$$

9. Boil some cochineal insects in water to which some alum has been added, then drop in ammonium hydrate until the precipitation is complete. Filter and compare the filtrate with the original solution.

10. Boil some logwood chips in water until the liquid is quite brown. Dip a piece of white cotton in this; tear the cotton in two and dip one of the pieces, first into a solution of alum, then into a weak solution of ammonia; finally wash both pieces in warm water.

5.—Notes on Aluminium.

Occurrence.—This element is very widely distributed in combination. Some of the best known compounds are, as oxides, coloured by impurities,—emery, sapphire, corundum; as silicates,—clay, feldspar, mica and hornblende; as a fluoride, with sodium in cryolite; and as a hydrate in bauxite, $Al_2O_3 2H_2O$ and in diaspore $Al_2O_3 H_2O$.

Preparation.—The metal is obtained chiefly (1) by heating the hydrate with sodium, (2) by heating the chloride with sodium, (3) by heating the hydrate or oxide with carbon in an electric furnace.

Compounds.—The hydroxide $Al_2(OH)_6$ is obtained by precipitation from any of the soluble salts of aluminium with an alkaline hydrate, not in excess, an alkaline carbonate, or ammonium sulphide. The aluminium sul-

phide, if formed, is decomposed by water (ex. 8). **The oxide Al_2O_3 results from heating the hydrate. The oxide is soluble** in strong alkalies and forms with them *aluminates*, setting hydrogen free; thus it is acidic to strong bases, as in the case of other weak basic oxides of metals. It is basic to strong acids forming the chloride sulphate, etc.

The chloride cannot be obtained free from water by the action of hydrochloric acid on the metal, for though a chemical action goes on and hydrogen is set free with the formation of a soluble chloride, when this solution is evaporated, decomposition goes on and hydrochloric acid escapes, leaving the oxide behind, thus :

$$Al_2Cl_6 + 3H_2O = Al_2O_3 + 6HCl.$$
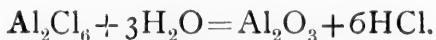
The chloride is prepared by heating a mixture of the oxide and charcoal in a current of chlorine. Neither the carbon nor the chlorine will reduce the oxide alone. $Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO.$

A hydrated chloride, $Al_2Cl_6 + 6H_2O$, can be obtained by treating the hydroxide with hydrochloric acid. (Compare magnesium.)

When an aluminium salt in solution has an alkaline hydrate added to it, the hydroxide is first precipitated, but this dissolves in excess of the reagent, forming an *aluminate* of the metal

$$Al(OH)_3 + 3M(OH) = Al(OM)_3 + 3H_2O \text{ when } M = K \text{ or } Na.$$
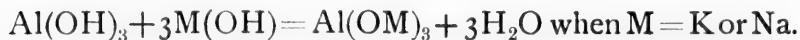
Similar compounds are formed with calcium, barium and strontium. Many of these aluminates occur native

and are known as *spinels*. Ortho-aluminates have the composition M_3AlO_3; meta-aluminates, $MAlO_2$. Compare boron, page 48.

Double Salts.—When aluminium hydroxide and an alkaline hydrate or carbonate are melted together an aluminate of the composition $AlOMO$ is obtained when $M = K$ or Na. This may be represented thus,—

$$O = Al - O - Na.$$
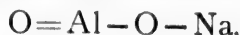
Similarly, aluminium chloride melted with a chloride of a strong base-forming element yields a double chloride, thus :—

$$Al_2Cl_6 + 2KCl = Al_2K_2Cl_8 = 2AlKCl_4, \text{or } Cl_2 = Al - Cl_2 - K.$$
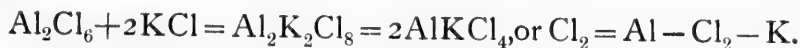
Of these double salts the sulphates form the most important compounds of aluminium. They have the composition

$$Al_2M_2(SO_4)_4 + 24H_2O = Al_2(SO_4)_3M_2SO_4 + 24H_2O.$$
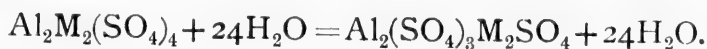
These are the *alums*. This name is given to a group of double sulphates, resembling each other in composition, in crystallization and in their chief physical properties. The type is

$R_2M_2(SO_4)_4 + 24H_2O$, and in ordinary alums.

$R = Al$, Fe, Cr or Mn, and $M = K$, Na or NH_4.
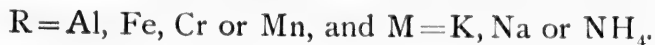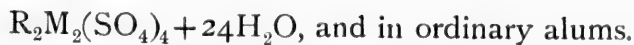
Silicates.—Among metamorphic rocks silicates of aluminium are abundant, two of the most common being feldspars, that have the composition $KAl(SiO_4)_2$ and $NaAl(SiO_4)_2$. From the decomposition of these through atmospheric influence arises the insoluble aluminium silicate, *clay*.

Experiments 9 and 10 illustrate the use of aluminium salts in fixing dyes. One of the common industrial uses of these salts is as *mordants*, that is, substances fixing or making fast colouring matters.

6.—Tests.

Borates.

(1) Treat with any strong acid, which displaces the boric acid, dissolve this in alcohol, ignite the solution,— flame green.

(2) Moisten the salt first with sulphuric acid, then with glycerine, after heating to drive off excess of the acid. When ignited, green flame appears.

(3) Borates impart a red colour to turmeric paper, when dry.

Aluminium.

(1) Alkaline hydroxides precipitate $Al_2(OH)_6$, slightly gelatinous, soluble in excess of the alkali except when ammonium is used (compare zinc).

(2) Sulphuretted hydrogen does not precipitate the sulphide.

(3) Ammonium sulphide precipitates $Al_2(OH)_6$ with free H_2S.

(4) Ignite the powdered salt on charcoal, then moisten the mass with cobaltous nitrate, $Co(NO_3)_2$; again ignite and a bright blue colour will appear.

7.—Questions and Exercises.

1. Prepare a bead of borax on a platinum loop. Do this by bending a loop about one-eighth of an inch in diameter on the end of a bit of wire. Heat this, and while still red, dip it in some powdered borax, fuse the borax, until it forms a transparent bead the size of the loop. Take up on this bead just a trace of copper oxide and hold it in the oxidizing flame (the outer tip of a bunsen flame will do). Note the colour the bead becomes when hot,—when cold. Clean the wire by crushing the cold bead by a blow on a flat plate. Repeat the experiment, using instead of copper, iron rust, manganese dioxide, and bichromate of potash, separately. Take only the smallest portion of the salt in each case.

2. Try if other alkaline sulphides than that of ammonium will precipitate $Al_2(OH)_6$ from a solution of a salt of aluminium.

3. Add sodium carbonate to alum solution, filter off the precipitate, and test it for a carbonate. Compare the result with that similarly obtained from magnesium and zinc.

4. When a soluble aluminate is treated with a chloride of one of the metals of the calcium group an insoluble aluminate is thrown down, thus : $2NaAlO_2 + CaCl_2 = 2NaCl + Ca(AlO_2)_2$. What is the valence of the radical AlO_2 ?

5. Try if a barium salt, when wet with sulphuric acid will give the characteristic green flame.

6. Aluminium hydrate when ignited yields the oxide ; what other metals have been found capable of the same reaction ? Have any been found in which this was impossible ?

7. Compare the action of strong alkalies on alumina and on zinc.

8. When an alkaline carbonate is added to an aluminium salt the hydroxide is precipitated and the carbon dioxide is given off. Compare the corresponding results in the cases of magnesium and zinc.

CHAPTER VIII.

LEAD GROUP.

1.—Carbon, Silicon, Tin, Lead.

Carbon is a non-metallic element existing in three entirely different forms, graphite, amorphous carbon and diamond. It forms oxides CO and CO_2, the latter only being acidic. With hydrogen it forms a great number of volatile compounds.

Silicon is either an amorphous grey powder, or a crystalline metallic looking substance. It is non-metallic in so far as its oxide and hydroxide are acidic, never basic, so that salts of silicon are unknown. The only oxide is SiO_2, and the hydride is SiH_4.

Tin, a soft white metal, oxides basic and with strong bases weakly acidic. It forms both stannous and stannic salts, having the type composition $SnCl_2$ and $SnCl_4$.

Lead, a soft, slightly bluish coloured metal, oxides are generally basic and form two series of salts, plumbous and plumbic. The former are far commoner than the latter. With strong bases the peroxide PbO_2, acts acid.

As the acid properties of the oxides of these elements decrease, so does the stability, thus: CO_2, SiO_2, SnO_2, PbO_2. The first is not at all basic and is very stable, the last is scarcely at all acidic and is very easily decomposed.

2.—Carbon.

Occurrence and Preparation.—The three forms of carbon are found as minerals. Two of these are crystalline, the diamond and graphite (plumbago). The other is amorphous and in the mineral form is coal ; prepared artificially it is charcoal, lampblack, etc. Charcoal is made from organic substances by heating under conditions which will not permit of combustion except of the gaseous constituents. Graphite has been obtained by mixing charcoal with molten iron. Charcoal burns easily when heated with oxygen ; the product is the dioxide, CO_2. When the supply of air is limited, the lower oxide, CO, is sparingly formed (compare phosphorus). Diamond burns, but with difficulty, the product again is the dioxide, with a trace of ash. Graphite burns, to carbon dioxide, but only at a very high temperature.

3.—Compounds.

Oxides.

Carbon forms two well known compounds with oxygen, the monoxide, CO, obtained by direct union, or by the reduction of some higher compound; and the dioxide, also formed either by reduction, or by direct union of its elements. The trioxide, C_2O_3 is unknown in the free state, but oxalic acid may be a union of this oxide with water, as shown by the decomposition with sulphuric acid, thus : $H_2C_2O_4 = H_2O + C_2O_3 = H_2O + CO + CO_2$.

The monoxide, CO, is obtained (*a*) by reducing the dioxide by red hot carbon, $C + CO_2 = 2CO$; (*b*) by reducing

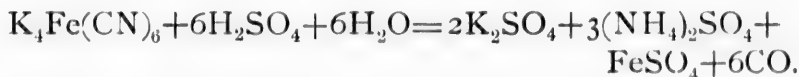metallic oxides by charcoal, $CuO + C = CO + Cu$. $ZnO + C = Zn + CO$.

$Fe_2O_3 + C = FeO + CO_2$, and $FeO + C = Fe + CO$;

(c) by reducing carbonates by metals, $CaCO_3 + Pb = PbO + CO + CaO$; (d) by decomposition of an oxalate by strong sulphuric acid

$H_2C_2O_4 + H_2SO_4 = (H_2SO_4 + H_2O) + (CO + CO_2)$;

(e) by the action of sulphuric acid on ferrocyanide of potash.

$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO$.

Carbon dioxide, CO_2, is obtained by (a) heating carbon in oxygen; (b) by displacing the metallic oxide from a carbonate by any strong acid

$MCO_3 + 2HCl = MCl_2 + H_2CO_3 = MCl_2 + H_2O + CO_2$;

(c) by decomposing by heat the carbonates of some of the metals, such as those of the calcium group, zinc, magnesium, manganese, etc. ; (d) by the oxidation of carbonic oxide.

Carbonic acid.

Carbon dioxide is readily soluble in water, and the solution is thought to be a chemical compound, H_2CO_3, carbonic acid.   When an attempt is made to isolate the acid it is decomposed into water and carbon dioxide. This accounts for litmus paper that has been reddened by this solution turning blue when dry, and for solution

of litmus that has been reddened by a current of the dioxide gas, turning blue when boiled. This acid being dibasic, of course, forms two series of salts,—acid and normal. If carbon dioxide be added to the neutral carbonate of an alkali, the corresponding acid carbonate is formed. This accounts for the disappearance of the precipitated carbonates of the metals of the calcium group, when an excess of the dioxide is passed into the solution, thus: $H_2O + CO_2 = H_2CO_3$, and $H_2CO_3 + Ca(OH)_2 = CaCO_3 + 2H_2O$. Then $CaCO_3 + nH_2O + CO_2 = CaH_2(CO_3)_2 + (n-1)H_2O$. This acid salt is soluble, and is known only in solution; for if the solution be boiled, CO_2 passes off and the precipitate reappears. The acid salt is also decomposed by caustic alkalies, with the precipitation of the original carbonate, together with the new one formed if it is insoluble. $CaH_2CO_3 + 2K(OH) = CaCO_3 + K_2CO_3 + 2H_2O$.

Carbon dioxide, as the ultimate product of carbon combustion, is incombustible. It does not support combustion either, in the ordinary sense, though some substances, such as carbon, sodium, hydrogen and magnesium, when heated to a high temperature decompose the gas either into the monoxide and oxygen or into its elements, and form combinations with the oxygen thus freed.

Hydrides and Hydrogen Compounds.

With hydrogen, carbon forms a great number of compounds. The valency of carbon is four with reference to hydrogen, but the compounds do not always show this, for example CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc., are the hydro-

carbons in one series; while C_2H_4, C_3H_6, C_4H_8, etc., form another series, and C_2H_2, C_3H_4, C_4H_6, etc., make up a third series. In the first the general formula is CnH_2n+_2; in the second, CnH_2n; and in the third, CnH_2n-_2. The starting point of the first series is methane, that of the second ethylene, and of the third acetylene. The bonds of the valency of carbon are accounted for by the carbon atoms of the molecules uniting with themselves. Thus:

First series,

$$
\begin{array}{ccc}
\mathrm{H} & \mathrm{H}\ \ \mathrm{H} & \mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}\\
\mid & \mid\ \ \mid & \mid\ \ \mid\ \ \mid\\
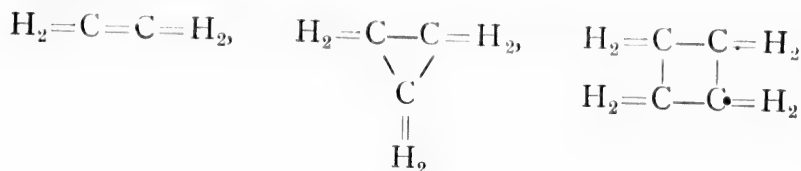\mathrm{H-C-H}, & \mathrm{H-C-C-H}, & \mathrm{H-C-C-C-H}\\
\mid & \mid\ \ \mid & \mid\ \ \mid\ \ \mid\\
\mathrm{H} & \mathrm{H}\ \ \mathrm{H} & \mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}
\end{array}
$$

Second series,

$$
\mathrm{H_2=C=C=H_2}, \qquad \mathrm{H_2=C-C=H_2}, \qquad \mathrm{H_2=C-C=H_2}
$$

$$
\begin{array}{c}
\backslash\ \ / \\
\mathrm{C}\\
\parallel\\
\mathrm{H_2}
\end{array}
\qquad
\mathrm{H_2=C-C=H_2}
$$

Third series,

$$
\mathrm{H-C=C-H}, \qquad \mathrm{H-C=C-H}, \qquad \mathrm{H-C=C-H}
$$

$$
\begin{array}{c}
\backslash\ \ /\\
\mathrm{C}\\
/\ \ \backslash\\
\mathrm{H}\ \ \ \mathrm{H}
\end{array}
\qquad
\begin{array}{c}
\mathrm{H=C-C=H}\\
\mid\ \ \mid\\
\mathrm{H}\ \ \mathrm{H}
\end{array}
$$
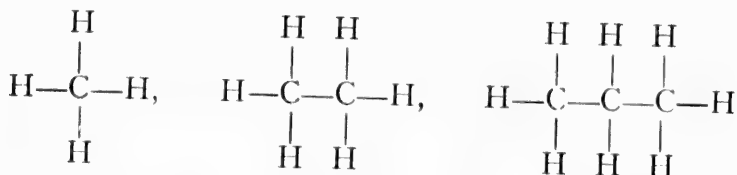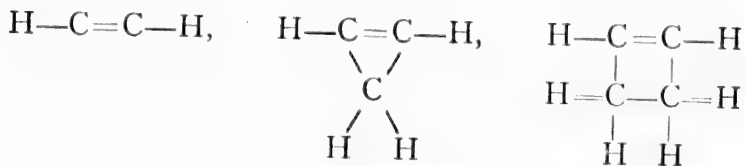
The hydrogen in these compounds is replaceable either in whole or in part by other elements, thus starting with CH_4, there may be formed (a) CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4; (b) $CH_3(OH)$, $CH_2(OH)_2$, $CH(OH)_3$,

$C(OH)_4$; (c) CH_2O, CO_2. In (a) the hydrogen is replaced atom by atom by chlorine, in (b) the replacing substance is hydroxyl, and (c) shows two oxidation products of marsh gas.

Sulphide.

Just as carbon and oxygen, when heated unite to form the dioxide, so carbon and sulphur when heated, combine to form the disulphide. In the case of the sulphide, however, the action analogous to the decomposition of the carbonate does not occur, because of the greater stability of the sulphur acid and its salts. The oxides of hydrogen and of carbon unite to form carbonic acid, which exists only in solution, yet forms salts readily, having the composition M_2CO_3, when M is a monad base. The sulphides of hydrogen and of carbon do not directly unite, but an acid having the composition H_2CS_3 sulpho-carbonic acid or thio-carbonic acid, is known. It is prepared by acting upon sodium sulpho-carbonate (thio-carbonate) with hydrochloric acid. $Na_2CS_3 + 2HCl = Na_2Cl + H_2CS_3$. The salt Na_2CS_3 is obtained by treating sodium sulphide Na_2S with carbon disulphide, thus $Na_2S + CS_2 = Na_2CS_3$. Sulpho-carbonates of the alkalies are known, as Na_2CS_2, K_2CS_3, $CaCS_3$, etc. The sulphur analogue of carbonic oxide has not been investigated. When CO_2 and CS_2 have one atom of oxygen and of sulphur respectively replaced by chlorine the resulting compounds are $COCl_2$ carbonyl chloride or oxychloride of carbon, and $CSCl_2$, sulpho-carbonyl chloride, or thio-carbonyl chloride. Also, in CO_2 when one atom of oxygen is replaced by sulphur there is formed carbonyl sulphide, COS. The preparation is similar to that of

CO_2 from CO, viz., by heating carbon monoxide and sulphur together.

Compounds with Nitrogen.

Carbon forms with nitrogen one very important compound, cyanogen, CN. (Sometimes the formula is contracted to Cy.) The group CN acts as a monad radical, thus KCN is cyanide of potassium. When KCN is treated with a strong acid, it decomposes and forms hydrocyanic (prussic) acid, one of the most violent poisons known. Oxide of hydrogen with one atom of hydrogen replaced by cyanogen forms cyanic acid, $H(CN)O$. Similarly sulphide of hydrogen with one atom of hydrogen displaced by cyanogen becomes sulpho-cyanic acid $H(CN)S$. The salts of these acids are respectively cyanates, such as KCNO, and sulphocyanates, as KCNS. $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, or $K_6Fe_2(CN)_{12}$ are respectively the ferrocyanide and ferricyanide of potassium; that is, they are both double cyanides of potassium and iron; but in the former, iron is a diad; in the latter, a triad. See under Iron.

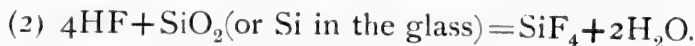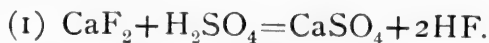Since cyanogen has a valency of one it is believed to have the composition $- C \equiv N$.

In its combinations with hydrogen and the alkalies cyanogen resembles chlorine. Carbon and nitrogen do not unite directly, cyanogen being obtained as a reduction product.
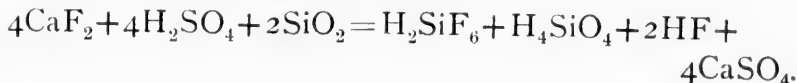

4.—Silicon.

EXPERIMENTS.

1. Powder some broken glass in a mortar (powdered quartz will answer as well), mix this with an equal quan-

tity of fluor spar, also powdered. Put the mixture into a flask fitted with a cork and delivery tube which dips into some mercury in a beaker. Pour water into the beaker above the mercury, and sulphuric acid into the flask. Heat the flask. A gas should come off which in the water forms a gelatinous solution. Filter this solution; save both the filtrate and the solid on the paper. The clear fluid is hydro-fluosilicic acid, H_2SiF_6, and the pasty substance on the paper is silicic acid H_4SiO_4. The reactions are :—

(1) $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$.

(2) $4HF + SiO_2$(or Si in the glass)$= SiF_4 + 2H_2O$.

(3) $SiF_4 + 4H_2O = H_4SiO_4 + 4HF$.

(4) $SiF_4 + 2HF = H_2SiF_6 = 2(HF)SiF_4$.

These may be summed up thus :—

$$4CaF_2 + 4H_2SO_4 + 2SiO_2 = H_2SiF_6 + H_4SiO_4 + 2HF + 4CaSO_4.$$

2. To the hydro-fluosilicic acid of the last experiment add potassic hydrate until it is neutralized, then evaporate. Fluosilicate of potassium $K_2SiF_6 = K_2F_2SiF_4$ results.

3. In a hard glass tube, heat to bright redness some potassic fluosilicate mixed with metallic sodium,—about equal weights of the two should be used. After cooling, wash out the brown residue and collect it on a filter paper. It is silicon.

$$K_2SiF_6 + 4Na = 4NaF + 2KF + Si.$$
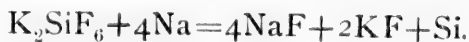
4. Heat a little of this powder in air.

5. Heat some of the silicic acid to bright redness.

$$H_4SiO_4 = SiO_2 + 2H_2O.$$

6. Fuse some sodium carbonate and finely powdered quartz, let the former be largely in excess of the latter. After all gas has ceased to come off let the mixture cool and try it for solubility.   Is it acid?

$$2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2.$$

The Na_4SiO_4 is sodium silicate or soluble glass.

7. Drop into the solution of the sodium silicate some hydrochloric acid.

$$Na_4SiO_4 + 4HCl = 4NaCl + H_4SiO_4.   \text{(See ex. 1.)}$$
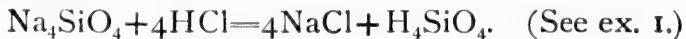
5.—Notes on Silicon.

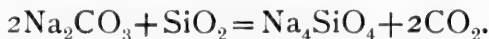**Occurrence.**—Silicon is never found free on account of its ready oxidation.   In combination, though, it forms a large percentage of the solid part of the earth.   Sand and sandstone, flint and all varieties of quartz are forms of silica, that is silicon dioxide.   Feldspar, serpentine and mica are silicates, while hornblende and clay are silicon compounds.

Preparation and Varieties.—Like carbon, silicon exists in three forms: (*a*) the amorphous form, a brown powder prepared as in ex. 3; (*b*) crystallized silicon, prepared by heating together potassic fluosilicate, sodium and zinc.   The first two substances interact as in ex. 3, while the zinc in the molten state dissolves the silicon.   This forms crystals on cooling, and the mass is

treated with hydrochloric acid to dissolve away the zinc. The silicon crystals are left in the form of prismatic needles; (c) when the solvent is molten aluminium instead of zinc the silicon crystallizes in scales much resembling graphite.

Combinations.

Oxides and Hydroxides.—There is said to be a monoxide of silicon SiO, but its existence does not seem to be established beyond question.

The sesquioxide Si_2O_3 is known and is of interest as showing the relations of silicon to other elements.

Silicon dioxide SiO_2, occurs in nature as quartz.

The hydrate corresponding to the dioxide is $Si(OH)_4$ $= H_4SiO_4$, silicic acid.

Other Compounds.—The monosulphide SiS, is obtained from the disulphide SiS_2.

The disulphide is prepared by passing vapour of carbon disulphide over heated silicon.

The tetrachloride $SiCl_4$, is formed when chlorine is passed over a mixture of silicon and carbon.

Silicic Acid and Silicates.—Silicic acid, like carbonic acid, is known only in solution, for attempts to isolate it always have ended in decomposing it. Its salts are both very numerous, important and stable. Silicates of sodium potassium, aluminium and calcium form many valuable minerals, such as the feldspars, micas, serpentine, hornblende, the zeolites, etc.

In the arts, silicates are of importance because a mixture of them makes glass. The principal ones employed

5

for this purpose are those of sodium, potassium, lead and calcium.

Alkaline silicates are soluble, others are not.

Silicon hydride, SiH_4, a spontaneously inflammable gas, is prepared by acting on a mixture of silicon and magnesium with hydrochloric acid.

Silicon nitride Si_2N_3, is formed by heating silicon in a current of nitrogen. Compare boron and carbon.

6.—Tin.

EXPERIMENTS.

1. Examine a piece of tin,—not the sheet of the tin-smith's shop,—but a block of the metal. Cut it. Heat it on charcoal in the oxidizing flame. After the oxide cools, heat it again, either on the charcoal or on mica.

2. Try if a shaving of tin will dissolve in nitric acid, in hydrochloric acid, either when hot or cold. Try *aqua regia.*

3. If a little tin be melted and dropped into cold water, and then boiled with strong hydrochloric acid, it will dissolve very slowly and give off hydrogen. It is better to drop into the acid with the granulated tin some bits of platinum, which will be recovered unchanged when the operation is completed.

$2HCl + Sn = SnCl_2 + H_2$. $SnCl_2$ is stannous chloride.

4. Make a mixture of finely divided tin and mercuric chloride in a hard glass tube, and arrange that the vapour passing off may be received in a cooled condenser ; then heat. The liquid obtained is stannic chloride, $SnCl_4$.

5. Add hydrogen sulphide to the chlorides obtained in the last two experiments.

6. Make a solution of any tin salt and hang in it a piece of zinc. Repeat, using aluminium instead of zinc.

7. Heat together in a hard glass tube some fine tin filings, sulphur and ammonium chloride.

8. Add potassic chlorate to a solution of stannous chloride, and heat. Test for a stannic salt with hydrogen sulphide.

7.—Notes on Tin.

Occurrence and Preparation.—Tin is very rarely found native. The chief ores are the dioxide, SnO_2, called cassiterite, as a mineral; and tin pyrites, a mixture of sulphides of copper, iron and tin. The ore is first roasted to drive off sulphur, then reduced by heating with carbon.

Compounds.—Tin forms two series of compounds,— the stannous and the stannic. The types of these are $SnCl_2$, stannous chloride, and $SnCl_4$, stannic chloride.

Oxides.—When dichloride of tin, $SnCl_2$ is treated with an alkaline carbonate, an oxyhydrate of tin $Sn_2O(HO)_2$ is formed; this when dried out of contact with oxygen yields SnO, stannous oxide, a brown powder that readily burns to the dioxide, SnO_2. This latter substance when it occurs native is cassiterite—or tin-stone, when prepared artificially, it is stannic oxide.

When stannic chloride $SnCl_4$ has added to it a solution of potassic carbonate, the compound $SnO(HO)_2$ sepa-

rates. This is stannic acid. Possibly it may be $Sn(HO)_4$ with a molecule of water separated. It acts as a dibasic acid with strong bases, forming salts called stannates, of which K_2SnO_3 is an example.

Metastannic Acid.—Tin dissolved in strong nitric acid yields a compound having the formula $H_{10}Sn_5O_{15}$, of which the sodium salt is $H_8Na_2Sn_5O_{15}$.

Chlorides.—The stannous chloride, $SnCl_2$ is prepared as in ex. 3, or by heating tin in hydrochloric acid gas. When dissolved in excess of water oxychloride of tin $Sn_2OCl + H_2O$, is thrown down. Compare antimony. The dichloride is useful in chemistry as a reducing agent as it readily takes up chlorine from chlorides, and oxygen from water, thus setting free hydrogen. Stannic chloride $SnCl_4$ is obtained, either by the action of chlorine on molten tin, or by distilling tin with corrosive sublimate (ex. 4).

Sulphides.—Stannous sulphide SnS is obtained either by heating the elements together or by saturating a solution of a stannous salt with hydrogen sulphide. It is brown. Stannic sulphide, SnS_2, is prepared by heating tin and sulphur with ammonium chloride. It is yellow in colour. (Ex. 7.)

Just as stannic oxide with water forms stannic acid, so stannic sulphide with a soluble sulphide produces sulpho-stannic acid.

$$SnO_2 + H_2O = H_2SnO_3$$
$$SnS_2 + H_2S = H_2SnS_3.$$
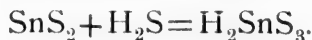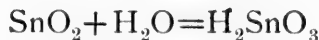
8.--Tests.

(*a*) A stannous salt treated with hydrogen sulphide yields a brown precipitate that is dissolved in yellow sulphides, in boiling hydrochloric acid, and in caustic potash solution. Stannic salts also yield a precipitate with hydrogen sulphide, but it is yellow and is soluble in sulphide solutions, in boiling hydrochloric acid, and in caustic potash.

(*b*) Alkaline carbonates precipitate hydroxides. The precipitate is not soluble in ammonium hydrate or carbonate.

9.--Lead.

EXPERIMENTS.

1. Heat a bit of lead on charcoal in the oxidizing flame.

2. Mix some oxide of lead with powdered charcoal and heat in the reducing flame.

3. Heat some galena, PbS, in an open tube of hard glass. What gas is given off?

4. Heat some monoxide of lead, PbO, (yellow oxide) with nitric acid, evaporate a little of the solution. The salt is nitrate of lead, $Pb(NO_3)_2$.

5. Make a solution of acetate of lead and add some acetic acid. Hang in this a strip of clean zinc for a few hours, then scrape off the metallic deposit, wash it, and examine it. Is it zinc? Is it tin?

6. Boil some lead filings with sulphuric acid. After

cooling, add water, and filter off the precipitate.   Is it a sulphate ?   Is it soluble ?

7. To a solution of lead nitrate, add some sodium carbonate.   Is the white powder a carbonate ?

8. Heat some of the white powder of the last experiment.

9 Heat some lead filings strongly in a current of oxygen.   Compare the result with that of the last experiment.

10. Heat some of the red or the brown oxide of lead in a current of hydrogen in a hard glass tube.

11. Make a strong solution of chlorine and shake up with separate portions of it some red oxide and some yellow oxide of lead, then let it stand for some hours.

12. Make a solution of a lead salt, divide it into three portions.   Into one, pour slowly a little sodium hydrate ; into another, some ammonium hydrate ; and into the third, some potassium hydrate.   Then add to each excess of the hydrate first put into it.

13. Heat some red oxide of lead, Pb_3O_4, with nitric acid, until it turns brown, then filter.   The brown powder is lead dioxide or peroxide, PbO_2.   Will the yellow oxide, PbO, give a similar result ?   Test the filtrate with hydrochloric acid.

14. Warm some of this peroxide with sulphuric acid and try if oxygen is given off.   Compare manganese dioxide.

15. Pass hydrogen sulphide through a solution of a lead salt made acid with acetic acid.   Is the precipitate soluble in ammonia ?

16. Add to a solution of a lead salt (acetate) a little hydrochloric acid. Is the precipitate soluble in ammonia? In nitric acid? Is it soluble in boiling water?

17. Add a little solution of potassic iodide to a solution of a lead salt.

18. Make a solution of a lead salt and drop into it some bichromate of potash solution. This gives chrome yellow $PbCrO_4$.

19. Drop some solution of magnesic sulphate into a clear solution of a lead salt.

20. Try if lead monoxide is soluble in hot caustic potash solution, in hydrochloric acid, in nitric acid.

21. Make a mixture of powdered chlorate of potash and lead monoxide, then heat sufficiently to decompose the chlorate. This when well washed on a filter should yield a brown powder, PbO_2.

10.—Notes on Lead.

Occurrence and Preparation.—Many lead compounds are found as minerals, the chief of these are the sulphide (galena), the carbonate and the sulphate. The first is the most important ore, and the lead is obtained by roasting to drive off part of the sulphur and alter the rest into the sulphate. The monoxide is formed to some extent at the same time. This mixture is then strongly heated and yields lead and sulphur dioxide.

$$2PbO + PbSO_4 + 2PbS = 5Pb + 3SO_2.$$
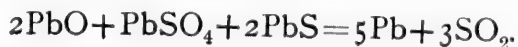
Compounds.

Oxides.—Lead forms the following oxides : the sub-oxide, Pb_2O ; the monoxide, PbO ; the sesquioxide, Pb_2O_3 ; the tetroxide (red lead), Pb_3O_4 ; and the dioxide or peroxide, PbO_2.

The *monoxide*, PbO results from direct union of the elements, when lead is heated to redness in presence of oxygen.   It may also be obtained by heating the hydrate of lead in carbon dioxide, or by reducing the carbonate or the higher oxides, either by heating, or in a current of hydrogen.   When prepared without being allowed to fuse it is a yellow powder, and is known as *massicot*. When fused it forms a reddish mass called *litharge*.   The monoxide is soluble in boiling alkaline hydrates, and forms salts with acids.   With water it reacts alkaline because it forms a hydroxide.

The *suboxide*, Pb_2O is formed, as a black powder, when oxalate of lead is heated in an atmosphere of nitrogen. It yields lead salts and free lead with acids, thus :—

$$Pb_2O + 2HNO_3 = Pb(NO_3)_2 + H_2O + Pb.$$
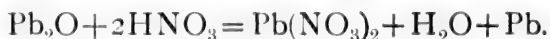
The *sesquioxide* Pb_2O_3 is obtained by precipitating by dilute ammonium hydrate, a solution of red lead in acetic acid, or by acting with sodium hypochlorite on an alkaline solution of a lead salt.   Practically it is of little importance ; theoretically it is interesting because it may be the lead salt of an acid of lead, $H_2PbO_3 = PbO(OH)_2$, plumbic acid.   The salt would then be $PbPbO_3$.

The tetroxide, Pb_3O_4, *red lead* or *minium*, is formed by continuous heating of the monoxide in presence of oxygen.   It has been sometimes regarded as a mixture

of the monoxide and dioxide, thus, $(PbO_2)2PbO$. The objection to this view is that solvents of the monoxide do not dissolve any of the red lead.

The *peroxide or dioxide*, PbO_2, is obtained (*a*) by heating the monoxide with strong oxidizing agents, such as potassic chlorate, or potassic nitrate ;

$$3PbO + KClO_3 = 3PbO_2 + KCl.$$
$$PbO + KNO_3 = PbO_2 + KNO_2.$$

(*b*) By acting on red lead with dilute nitric acid

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

Sulphuric acid, when used, yields the sulphate instead of the nitrate.

(*c*) By the action of chlorine or hydrogen dioxide on lower oxides suspended in water

$$PbO + H_2O + 2Cl = PbO_2 + 2HCl.$$

(*d*) By fusing lead monoxide and caustic soda, thus,—

$$PbO + 2NaOH = PbO_2 + Na_2O + H_2.$$

It is a brown powder, that has strong oxidizing properties. When heated it decomposes thus,—$2PbO_2 = 2PbO + O_2$. To reducing agents, such as hydrogen, and sulphurous acid, it yields oxygen

$$PbO_2 + H_2 = H_2O + PbO.$$
$$PbO_2 + H_2SO_3 = PbSO_4 + H_2O.$$
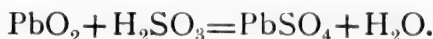
With nitrogen tetroxide and sulphur dioxide it yields respectively lead nitrate and sulphate, thus :—

$$PbO_2 + 2NO_2 = Pb(NO_3)_2, \text{ and } PbO_2 + SO_2 = PbSO_4.$$
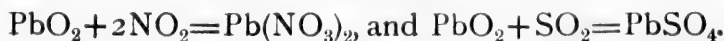
With hydrochloric and sulphuric acids it acts just as manganese dioxide does, $PbO_2+4HCl=PbCl_2+2H_2O+Cl_2$, and $PbO_2+H_2SO_4=PbSO_4+H_2O+O$.

If one atom of oxygen be replaced by hydroxyl, plumbic acid is formed, $PbO(OH)_2=H_2PbO_3$. When lead dioxide is fused with excess of a caustic alkali, and the product dissolved, a hydrated plumbate is obtained, thus :—

$$PbO_2+2KOH=K_2PbO_3+H_2O.$$

This is the lead salt analogous to the stannate. (Compare tin dioxide, page 68.)

Sulphide.—The native sulphide of lead is galena, which crystallizes in cubes, the artificial sulphide, prepared by the action of hydrogen sulphide on a lead salt is amorphous.

Chlorides.—The dichloride $PbCl_2$ may be prepared by the action of hydrochloric acid on a solution of a lead salt, or by the action of hydrochloric acid on the oxide. It is soluble in boiling water and in strong hydrochloric acid. Chlorine passed into the solution turns it reddish in colour. If water or an alkaline solution be added, lead peroxide is precipitated ; but if the red solution be heated chlorine is set free. This makes it probable that the red substance is a higher chloride of lead, the tetrachloride, $PbCl_4$, which is unstable, and exists only in a somewhat concentrated solution, being decomposed either by heating or diluting.

$$PbCl_2+Cl_2=PbCl_4$$
$$\text{and } PbCl_4+2H_2O=PbO_2+4HCl.$$

Other *halides* are formed similar to the dichloride; that with iodine being bright yellow. A number of basic chlorides of lead are known, having such composition as $PbO \cdot PbCl_2$ and $PbO \cdot PbOCl_2$.

Sulphate.—Lead sulphate is scarcely at all soluble in water (compare barium sulphate). It is precipitated from lead salts by sulphuric acid or soluble sulphates. It is dissolved by most ammoniacal salts and by calcic acetate, also slightly by concentrated sulphuric acid.

Nitrate.—The nitrate is obtained by dissolving the oxide or carbonate in nitric acid. It is readily soluble in water but not in nitric acid.

Carbonate.—The normal carbonate $PbCO_3$ occurs as a mineral, and may be prepared artificially, but is unimportant. Basic carbonate of lead, the *white lead* of commerce, requires mention. It is prepared either by acting on sheet lead, in presence of air, with acetic acid, thus forming a basic acetate, then passing in carbon dioxide to change the acetate into carbonate; or by boiling oxide and acetate together, then passing carbon dioxide into the solution of what is probably a basic acetate. White lead is a mixture of basic carbonates; one of the simplest of these is $PbCO_3.Pb(OH)_2$.

11.—Tests.

(*a*) A white precipitate in cold concentrated solutions with hydrochloric acid. Precipitate dissolved by boiling.

(*b*) A black precipitate (red in excess of HCl) with hydrogen sulphide. Precipitate insoluble in potassic

hydrate or ammonium sulphide ; but soluble in boiling nitric acid.

(*c*) White precipitate with sulphuric acid, somewhat soluble in water, but very slightly so in dilute acid.   Precipitate soluble in boiling hydrochloric acid.

(*d*) A yellow precipitate with potassium bichromate, soluble in caustic potash, insoluble in acetic acid.

(*e*) A precipitate formed with soluble hydrates, which is itself soluble in excess of either potassic or sodic hydrate, but not in that of ammonium.

(*f*) The characteristic colouration of the flame, when a lead salt, previously dipped in HCl is held in the flame on a platinum loop.

———

12.—Questions and Exercises.

1. If red lead and bleaching powder be mixed and shaken up with water, then a little acid added, what chemical actions will take place ?   Write the equations.

2. Will chlorine displace the iodine in lead iodide?   Try by substituting lead iodide for red lead in the last question.

3. Lead sulphide is decomposed by heat in presence of air ; is dissolved by hydrochloric acid ; and is changed into the sulphate by nitric acid.   Write equations for the first and last of these actions. How could it be determined whether the sulphide is simply dissolved by the hydrochloric acid, or whether it forms a chloride?

4. Assuming that lead tetrachloride is produced by passing chlorine into the dichloride solution, what would be the result of adding stannous chloride ?

5. Write the formulæ for carbonate, silicate, stannate and plumbate of potassium, and compare them.

6. Make a tabulated list of the formulæ of the chief compounds of silicon, tin and lead. Carbon is frequently joined with this group. What reasons are there for the arrangement?

7. Lead salts are generally isomorphous with those of barium. What does this mean? What other points of resemblance between these metals?

8. Mix some barium dioxide and lead monoxide, add some water and pour into the whole some hydrochloric acid. Let the mixture stand for several hours, but shake it up frequently to keep the powder in suspension. Explain the reactions, with equations.

9. Try what result will follow when the monoxide of lead is shaken up with chlorine water, and let stand for a few hours. Will red lead be similarly affected?

10. If stannous chloride be added to solution of permanganate of potash what will occur?

11. Starting with lead, tin, silicon and carbon, how could the dioxide be obtained in each case?

12. Mix some monoxide of lead in a strong solution of carbon dioxide gas in water. After an hour or two, filter and dry the solid. Does it contain a carbonate?

CHAPTER IX.

1.—Nitrogen Group.

The members of this group are nitrogen, phosphorus, arsenic, antimony, bismuth.

The elements composing this family form the connecting link between the metals and non-metals. Nitrogen and phosphorus have no characteristics of metals; arsenic and antimony resemble metals in appearance, but their

oxides are acid forming; bismuth is metallic in appearance and properties, and its oxides are basic.

Phosphorus and arsenic exhibit allotropy ; and all the members of the group except bismuth form hydrides of the type MH_3. The chief chlorides have the type formulæ MCl_3 and MCl_5, and the oxides, M_4O_6, M_2O_4 and M_2O_5, except that in the case of arsenic AS_2O_4 is unknown.

2.—Phosphorus.

EXPERIMENTS.

1. Dissolve a little piece of phosphorus in carbon bisulphide ; spread the solution over a piece of soft paper and expose to the air.

2. Make a solution of phosphorus in carbon disulphide and allow the liquid to evaporate.   Examine the residue for crystals.

3. Make strong, solutions of silver nitrate and copper sulphate, put a piece of freshly cut phosphorus in each and allow them to stand for a couple of days.   Then examine the deposits.

4. Determine the melting point and the ignition temperature of phosphorus, by placing a little piece in a test-tube half full of water, then immersing this tube nearly to the lip in a beaker of water, and applying heat to the latter.

5. Place a piece of phosphorus half as large as a pea on a bit of sheet zinc, set this on an earthenware or metal plate, ignite it, and invert over it a dry bell jar.   After

the white fumes have settled as a coating on the glass and plate, quickly scrape the deposit into a dry bottle and stopper tightly. Dissolve some of this white substance in a very little cold water, test for acid properties; also test it with silver nitrate solution. The white deposit is phosphorus pentoxide or phosphoric anhydride.

$$2P + 5O = P_2O_5 \text{ and } P_2O_5 + H_2O = 2HPO_3 = 2PO_2(OH).$$
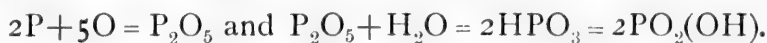
6. Make a little solution of the pentoxide in a test-tube and boil it for some time. Test again with silver nitrate.

$$P_2O_5 + 3H_2O = 2H_3PO_4 = 2PO(OH)_3.$$

7. Dilute some nitric acid to half its strength, then heat in this some phosphorus. After the phosphorus has dissolved, evaporate the solution until it begins to get thick, and test it with silver nitrate.

8. Nearly fill a small retort, of from a quarter to a half litre capacity, with a strong solution of caustic potash or soda; then drop in two or three small bits of phosphorus. Arrange the retort on a stand so that the mouth will dip under warm water in a large dish. The upper part cf the retort should be filled with some gas that does not support combustion, such as nitrogen or carbon dioxide. Instead of this a few drops of ether may be run in, and this will be vaporized, the vapour driving out the air. Apply heat until the contents boil briskly. The escaping gas should ignite on coming in contact with the air. Do not lift the mouth of the retort out of the dish until the condensing steam has drawn the water back to completely fill the retort. Collect a little of the gas in a test-tube over water and let it stand

for a day.   See if it will then ignite on coming in contact
with the air.   Try this by tipping the tube below water
so as to allow the gas to escape a little at a time.

$$4P + 3KOH + 3H_2O = PH_3 + 3KP(HO)_2.$$
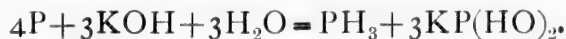
The PH_3 is phosphine or phosphuretted hydrogen.
KPH_2O_2 is potassium hypophosphite.

3.—Notes on Phosphorus.

Preparation.—Phosphorus is obtained from calcic
triphosphate, $Ca_3(PO_4)_2$, which occurs either as the
mineral apatite, or as the incombustible constituent of
bone.   The bones, when used for preparation of phos-
phorus are burned to drive off the animal matter, then
ground to powder.   The bone ash thus obtained is chemi-
cally the calcic salt of orthophosphoric acid, and has the
same composition as apatite.   Treated with sulphuric acid
it reacts as follows:—$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 +$
$2CaSO_4$.   Of the two substances thus obtained, the
calcic sulphate is almost insoluble, while the mono-calcic
phosphate is readily soluble.   They can, therefore, be
separated by filtering.

The filtrate is evaporated to dryness and heated to re-
duce it to the metaphosphate by expelling water.

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

The metaphosphate is next mixed with charcoal and
heated.   This reduces the salt thus :—

$$3Ca(PO_3)_2 + 10C = P_4 + 10CO + Ca_3(PO_4)_2.$$
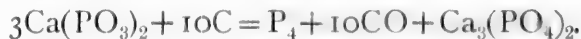
If sand, SiO_2, be added the metaphosphate is entirely reduced, thus:— $2Ca(PO_3)_2 + 10C + 2SiO_2 = 2CaSiO_3 + 10CO + P_4$. The phosphorus, in either case, distils over and is collected under water.

Allotropic Forms. — Common yellow phosphorus, when heated to 290° in a gas with which it will not unite chemically, becomes changed to red or amorphous (non-crystalline) phosphorus. In the presence of a small portion of iodine the change takes place at about 240°. The following is a comparative statement of the chief characteristics of these two forms:—Ordinary phosphorus,—waxy, translucent, readily oxidizes in the air, ignites at about 50°, luminous in the dark in presence of oxygen, insoluble in water, soluble in carbon bisulphide, very poisonous, non-conductor of electricity, sp. gr. 1.8 melts at 44°.

Red phosphorus,—a dark red powder, opaque, does not change in air, ignites at about 240°, not phosphorescent, insoluble in carbon bisulphide, conducts electricity, not poisonous, sp. gr. 2.38, melts at about 255°.

There is a third variety, known as metallic phosphorus, made by heating waxy phosphorus in a sealed tube with lead. It is a metallic looking substance in the form of scales.

4.—Oxides and Acids of Phosphorus.

Phosphorus forms four oxides, viz.: monoxide, P_4O; phosphorous oxide (trioxide), P_4O_6; tetroxide, P_2O_4; and pentoxide or phosphoric oxide, P_2O_5. Of these the phosphorous and phosphoric oxides are the important

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ones, because they are the anhydrides of the **two chief** acids of phosphorus. They are all obtained by **direct** union of the elements. When the supply of **air or** oxygen is in large excess, P_2O_5 is produced, but when the oxygen is in limited quantity in contact with the phosphorus, the other oxides are formed. P_4O is a reddish mass (resembling red phosphorus), remaining after a mass of P burns in a jar in presence of fumes of P_2O_5. P_4O_6 is sometimes called trioxide, because the formula was formerly written P_2O_3.

P_4O_6 yields with water H_3PO_3, phosphorous acid ; and P_2O_5 in a similar way forms H_3PO_4, orthophosphoric acid. H_3PO_4, by heating, loses water and becomes HPO_3, metaphosphoric acid ; so, $2H_3PO_4$ may part with one molecule of water and become $H_4P_2O_7$, pyrophosphoric, or diphosphoric acid.

The pentavalent hydroxide of phosphorus, $P(OH)_5$, is not known ; but the acids may be considered as derivatives from this hydroxide, thus :— $P(OH)_5 - H(OH) =$ $PO(OH)_3$, orthophosphoric acid. $PO(OH)_3 - H(OH) =$ $PO_2(OH)$. metaphosphoric acid. $2PO(OH)_3 - H(OH) =$ $(PO)_2O(OH)_4$, pyrophosphoric acid.

When one molecule of an ortho-acid parts with one molecule of water a meta-acid is formed, thus $H_3MO_4 -$ $H_2O = HMO_3$; and when two molecules of the ortho-acid part with one molecule of water, the result is a pyro-acid, thus, $2H_3PO_4 - H_2O = H_4P_2O_7$.

With the trivalent phosphorus atom is joined the hydroxyl group thus,— $P(OH)_3$, to form phosphorus acid. $HP(OH)_2$ is hypophosphorus acid, and $2PO(OH)_2$ is hypophosphoric acid.

Orthophosphoric acid is tribasic, and forms three classes of salts with monad bases, thus,—MH_2PO_4, M_2HPO_4 and M_3PO_4. The names of these respectively, assuming that M=sodium, would be dihydrogen sodium phosphate, or monosodium phosphate, disodium phosphate and neutral sodium phosphate. The atoms of hydrogen may be replaced by different bases, thus NH_4NaHPO_4 is microcosmic salt, or ammonium sodium hydrogen phosphate.

5.—Other Compounds.

Halides.—Phosphorus unites directly with the halogens to form compounds. For instance, chlorine acts on phosphorus to make the pentachloride, PCl_5, and this, when heated, decomposes into the trichloride and chlorine. Analogous reactions occur between all the members of the group and all the halogens, except in the cases of nitrogen, which does not unite directly to form the halide compounds, they being reduction products, and bismuth which does not form the pentachloride.

Phosphorus and Hydrogen.—Phosphorus with hydrogen forms three compounds. The best known of these is phosphine, PH_3, prepared as in experiment 7. This substance explodes spontaneously when mixed with air, if it is not purified from traces of another phosphide of hydrogen, P_2H_4, formed at the same time. This may be done by letting the gas stand in cold water, or by leading it through a cooled tube.

Sulphides of Phosphorus.—P_4S_3, P_2S_4, P_2S_5 are known. It will be noticed that the two latter ones are similar in

composition to two of the oxides. They do not, like the sulphides of arsenic and antimony, form sulph-acids, probably because hydrogen sulphide does not act chemically with phosphorus compounds.

6.—Vapour Density of Phosphorus.

Phosphorus boils at about 290°. The vapour density is 61.92 (62 nearly), hence at this temperature the molecular weight is 123.85, and since the atomic weight is 31, the molecule consists of *four* atoms. At very high temperatures the vapour density diminishes and the molecule is made up of only two atoms. (Compare sulphur.)

7.—Arsenic.

EXPERIMENTS.

1. Heat a bit of arsenic on charcoal in the oxidizing flame. Hold the charcoal so that the fumes will be blown along its surface. Observe the odour of these fumes and the colour of the coating they form on the charcoal.*

2. Try if arsenic will burn on mica. Use a small piece.

3. Heat in a small hard glass test-tube a bit of arsenic.

4. Make a bend of about half a right angle in a piece of hard glass tubing an inch from one end ; place a bit of arsenic in this tube at the bend, then hold the tube in a flame with the long arm nearly vertical. After all the

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* Do not use more of the arsenic than is necessary to give the reaction, and do not inhale more of the fumes than can be helped.

arsenic has disappeared, examine the coating with a magnifying glass. It should show vitreous diamond shaped (octahaedral) crystals of arsenious oxide, As_4O_6.

5. In a tube closed at one end, heat a mixture of arsenious oxide and powdered charcoal. Pass the escaping gas through lime water. Scrape off some of the deposit on the side of the tube and treat it as in ex. 1 and 2.

6. Try if arsenic trioxide is soluble in boiling water; use as a test silver nitrate solution. If soluble, a canary yellow precipitate of arsenite of silver will be obtained.

7. Boil some arsenious oxide in strong nitric acid. Evaporate to dryness, and dissolve some of the residue in water. Test this with nitrate of silver, and a brick-red precipitate of arsenate of silver is obtained.

8. Pass a current of hydrogen sulphide over some finely powdered and heated arsenic (the deposit on the tube in ex. 5 will answer well). The yellow compound is arsenic trisulphide, As_2S_3.

9. Dissolve some arsenious oxide in hydrochloric acid, and pass the solution through a funnel tube into a hydrogen generating apparatus from which hydrogen has been escaping for some time and has been ignited at the end of the delivery tube. Observe the altered colour of the flame. Smell the fumes. Hold a cold porcelain plate in the flame. (Preserve the plate with the coating on it.) While the gas is still escaping and burning, heat the delivery tube about six inches from the free end. Compare the deposit in the tube with that obtained in ex. 3. Did the flame of the burning gas alter
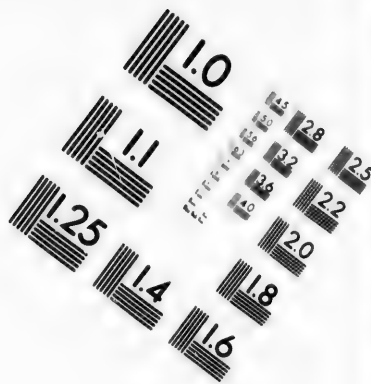
IMAGE EVALUATION
TEST TARGET (MT-3)
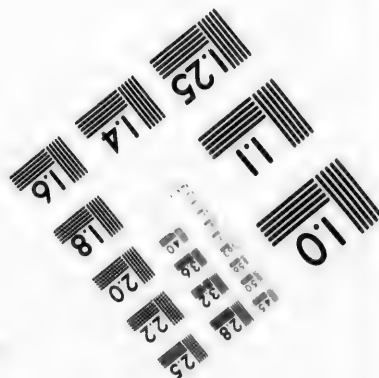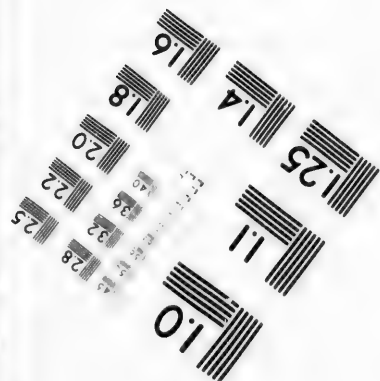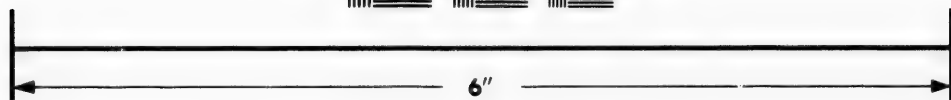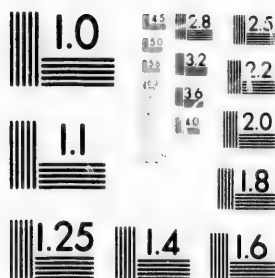
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at all during the heating of the tube? Cut off the tube behind the black ring (arsenic mirror) and hold in a flame, as in ex. 4. The gas that burned was Arsine, arseniuretted hydrogen or hydrogen arsenide, AsH_3. Write equations for the reactions throughout.

10. Try if hydrogen sulphide will form a precipitate in the hydrochloric acid solution of As_4O_6.

8.—Notes on Arsenic.

Occurrence and Preparation. — Arsenic occurs chiefly in arsenical pyrites, FeSAs. This substance may be considered as a bisulphide of iron, in which one atom of sulphur is replaced by arsenic.

Arsenic and Oxygen.—Arsenic, with oxygen, forms two compounds, As_4O_6 and As_2O_5,—the analogues of two phosphorous oxides. These are the anhydrides of arsenious and arsenic acids, H_3AsO_3 and H_3AsO_4 respectively.

The formula As_2O_3 and the name trioxide are retained in most books, but the vapour density of the substance is 197.7, this gives a molecular weight of 395.4 which corresponds to the molecular formula As_4O_6.

The solution of arsenious oxide in water gives arsenious acid, $As(OH)_3$, which has not been obtained apart from its solution. It yields well defined stable salts, however, both in the form of ortho-arsenites, M_3AsO_3, and met-arsenites, $MAsO_2$. Alkaline arsenites are soluble in water, others are not.

When arsenious oxide solution is oxidized it changes into a solution of arsenic acid, $AsO(OH)_3$, $O=As\equiv(OH)_3$,

thus $\quad As_4O_6+4HNO_3+4H_2O=4H_3AsO_4+2N_2O_3$;

or $\quad As_4O_6+10H_2O+8Cl=4H_3AsO_4+8HCl$.

The acid is obtained from its solution by evaporation. The ortho-acid, by heat, becomes changed into the pyro and meta-acids, $H_4As_2O_7=As_2O_3(OH)_4$, and $HAsO_3=AsO_2(HO)$ respectively.

9.—Tests.

The tests for an arsenite in neutral solution or for arsenious acid are, (1) nitrate of silver forms yellow arsenite of silver; (2) copper sulphate forms a green precipitate of cupric arsenite; (3) ferric chloride gives a brownish precipitate of arsenite of iron. If the solutions are not neutral, ammonia solution should be added.

10.—Arsenic and Hydrogen.

There are two compounds of these elements, AsH_3, Arsine, hydrogen arsenide or arseniuretted hydrogen, and As_2H_2, solid arsenide of hydrogen. The latter is of little importance. Arsine is formed by nascent hydrogen acting on arsenic, thus,—

$$Zn+H_2SO_4=ZnSO_4+2H$$
and $\qquad 24H+As_4O_6=4AsH_3+6H_2O$.
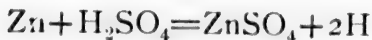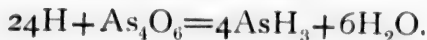
Also sulphuric acid acting on any arsenical metal yields AsH_3.

Arsine is important as a reducing agent, because it is readily decomposed, especially by heat, and both elements unite with oxygen. It is decomposed by the halogens, particularly by chlorine. With hot metals it forms arsenides and sets free hydrogen; thus, $2AsH_3 + 3K_2 = 2AsK_3 + 3H_2$. From salts of silver it precipitates the metal

$$4AsH_3 + 12Ag_2SO_4 + 6H_2O = 12H_2SO_4 + As_4O_6 + 12Ag_2.$$
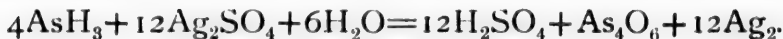
11.—Arsenic and Sulphur.

There are three compounds of these elements: the disulphide, As_2S_2; trisulphide, As_2S_3 and pentasulphide, As_2S_5.

As_2S_2, arsenic disulphide or realgar is a red sulphide of arsenic that occurs native. It may be prepared by heating the elements in proper proportions by weight, 9 to 4 nearly.

The disulphide, when treated with nitric acid, yields arsenic acid, free sulphur and oxides of nitrogen.

$$As_2S_2 + 6HNO_3 = 2H_3AsO_4 + 2S + 2N_2O_3 + 2NO_2.$$

As_2S_3, orpiment, arsenious sulphide or arsenic trisulphide, is prepared by passing hydrogen sulphide through a solution of arsenic trioxide, or over finely powdered and heated arsenic; or by heating together a mixture of arsenic trioxide and sulphur in proportion of 7 to 1. It is a yellow solid, see ex. 8.

Arsenic pentasulphide, As_2S_5, is formed by heating together arsenic trisulphide and sulphur.

The trisulphide and pentasulphide form acids, called the sulph-acids of arsenic, which are of the same type as the oxyacids, but the sulphur replaces the oxygen of the latter.

Sulphacids of Arsenic.—These compounds, known only by their salts, correspond to the oxyacids; thus, arsenious oxide dissolved in hydrogen oxide gives arsenious acid, H_3AsO_3, and arsenic trisulphide dissolved in hydrogen sulphide yields sulpharsenious acid, H_3AsS_3, or $HAsS_2$ (the meta-acid). Arsenious oxide with sodic hydroxide reacts as follows: $As_4O_6+4NaOH=4NaAsO_2+2H_2O$, yielding metarsenite of sodium and hydrogen oxide; so arsenic trisulphide with sulphydrate of sodium gives metasulpharsenite of sodium and hydrogen sulphide, thus,—$As_2S_3+2NaSH=2NaAsS_2+H_2S$.

When pentasulphide of arsenic is treated with an alkaline sulphide, or when a soluble arsenate is treated with hydrogen sulphide a sulpharsenate (thio-arsenate) is formed. $As_2S_5+Na_2S=2NaAsS_3$, metasulpharsenate of sodium,—$Na_3AsO_4+4H_2S=Na_3AsS_4+4H_2O$.

Arsenic and the Halogens.—Arsenic combines readily with the elements of the halogen group to form the trichloride, tribromide and tri-iodide. Simple contact, with heat in the case of chlorine, is sufficient to bring about the union.

12.—Antimony.

EXPERIMENTS.

1. Heat some powdered antimony in a closed tube. Compare the result with that obtained with arsenic.

2. Heat some of the antimony on mica.

3. Heat a bit of antimony on charcoal in the oxidizing flame.

4. Heat some antimony in a tube open at both ends, as with arsenic (ex. 4). Carefully compare the deposit in the tube with that obtained when arsenic was thus heated.

5. Try if oxide of antimony, when heated in a closed tube with charcoal, is reduced.

6. Use apparatus, as for the preparation of arsine, but instead of solution of arsenic, use a hydrochloric acid solution of tartar emetic, $K(SbO)(C_4H_4O_6)_2$. Treat the gas, stibine, SbH_3, that comes off as the arsine was treated (see ex. 9 under arsenic). Compare carefully the coating on the cold plate with that obtained from arsenic. Try to dissolve each in a solution of an alkaline hypochlorite.

7. Pass a current of stibine into a solution of potassic hydrate. This gives brown hydroxide of antimony $Sb(OH)_3$.

8. Pass a sulphide of hydrogen into solution of an antimony salt, or over finely divided antimony.

9. Drop some powdered antimony into strong nitric acid. The substance formed is Sb_2O_5.

10. Boil some antimony with strong hydrochloric acid that has added to it a very little nitric acid ; evaporate the solution to a syrup, then drop into cold water.

$$2Sb + 6HCl = 2SbCl_3 + 3H_2.$$
$$SbCl_3 + H_2O = SbOCl + 2HCl.$$
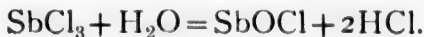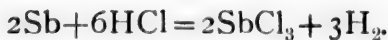
Decant the water and pour over the powder a strong solution of sodic carbonate.

$$4SbOCl + 2Na_2CO_3 = Sb_4O_6 + 4NaCl + 2CO_2.$$
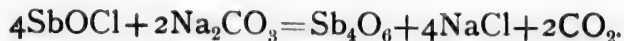
Again decant the liquid, pour over the powder a little strong nitric acid and heat gently. A yellowish powder Sb_2O_5 should be obtained, which is very slowly dissolved by hydrochloric acid.

13.—Notes on Antimony.

Occurrence.—Antimony is an ingredient of a large number of ores, but is chiefly obtained from the trisulphide Sb_2S_3, stibnite.

Antimony and Oxygen.—Three oxides of antimony are known. Sb_4O_6, antimonious oxide, is obtained by boiling antimony with sulphuric acid, then treating the sulphate with sodic carbonate, $2Sb + 3H_2SO_4 = Sb_2(SO_4)_3 + 3H_2$ and $2Sb_2(SO_4)_3 + 6Na_2CO_3 = Sb_4O_6 + 6CO_2 + 6Na_2SO_4$. The tetroxide, Sb_2O_4, is formed when antimony is burned in air and the oxides (Sb_4O_6 mixed with Sb_2O_4), strongly heated for some time. The tri-oxide thus oxidizes to the tetroxide.

Pentoxide of antimony is obtained by acting on antimony with nitric acid.

These oxides form antimonious and antimonic acids, H_3SbO_3 and H_3SbO_4, respectively. The former known by the salts corresponding to the meta-acid, thus $KSbO_3$, and the latter in the free state as the ortho-acid, $SbO(OH_3)$. The solution of antimonious oxide is

only weakly acidic, indeed to strong acids it is basic. Antimony forms two series of salts because of two forms of the hydroxide, both being bases ; thus, $Sb(OH)_3$ and $SbO(OH)$. In the former the antimony is trivalent, thus the sulphate is $Sb_2(SO_4)_3$; in the latter, the group SbO acts as a monad radical and forms a sulphate having the formula $(SbO)_2SO_4$. The salts formed by the trihydroxide are called *antimony* salts, those from the monohydroxide, *antimonyl* salts. The radical SbO corresponds to carbonyl, CO, and sulphuryl, SO, when these act as radicals.

The white powder formed in ex. 10 was oxychloride of antimony (powder of algaroth), or the chlorine compound of antimonyl.

A similar compound is $SbO_2Cl = (SbO)OCl$, formed by the action of water on pentachloride of antimony, thus $SbCl_5 + 2H_2O = SbO_2Cl + 4HCl$. This an oxychloride of antimonyl, as is the following,—$Sb_4O_5Cl = (SbO)_4OCl$.

14.—Antimony and Chlorine.

Antimony with chlorine forms a trichloride (butter of antimony), $SbCl_3$, as in ex. 10. If a current of chlorine gas be passed into the trichloride, it forms the pentachloride, $SbCl_5$. This, with cold water, produces antimonyl oxychloride, which with hot water forms antimonic acid ;

$$SbCl_5 + 2H_2O = SbO_2Cl + 4HCl,$$
$$SbO_2Cl + 2H_2O = SbO(OH)_3 + HCl.$$
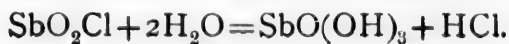
15.—Antimony and Sulphur.

When sulphide of hydrogen is passed into a solution of an antimony salt, trisulphide of antimony, an orange precipitate, is thrown down.

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$
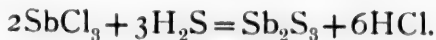
This sulphide forms salts of an acid that has the formula $SbS(SH)$ or $Sb(SH)_3$. The trisulphide (stibnite) occurs in nature as a black compound; when prepared artificially it is orange-coloured. The following chemical changes are produced by proper treatment :—

$$2Sb_2S_3 + 9O_2, \text{ when heated} = Sb_4O_6 + 6SO_2$$
$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$
$$2Sb_2S_3 + 4HNO_3 = Sb_4O_6 + 6S + 4NO + 2H_2O$$
$$Sb_2S_3 + 6H_2, \text{ when heated} = 2Sb + 3H_2S.$$
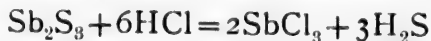
A pentasulphide Sb_2S_5 is also known.

16.—Tests.

(1) Orange precipitate with hydrogen sulphide, soluble in strong hydrochloric acid.

(2) The chloride gives white precipitate with water, soluble in tartaric acid.

(3) Antimony is distinguished from arsenic by these tests :—

> (a) The spots formed on the plate by burning stibine are sooty looking ;

(*b*) They turn orange when treated with **ammo-
nic sulphide** ;

(*c*) They are not dissolved by alkaline hypo-
chlorites.

17.—Bismuth.

EXPERIMENTS.

1. Compare bismuth with arsenic and with antimony
as to (1) physical properties, (2) burning in air, (3) solu-
tion in acids.

2. Dissolve some bismuth in strong nitric acid, and
evaporate to dryness, without unnecessary heat ; result-
ant powder is $Bi(NO_3)_3$, trinitrate of bismuth. $Bi +
4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O$.

3. Heat some nitrate of bismuth strongly, compare the
result with that obtained by burning the metal in air,
and with the coating on charcoal when bismuth is heated
in the oxidizing flame.

4. Treat some of the nitrate with solution of potassic
hydrate, $Bi(NO_3)_3 + 3KOH = Bi(OH)_3 + 3KNO_3$ If the
hydrate be strongly heated it changes into the oxide,
thus : $2Bi(OH)_3 = Bi_2O_3 + 3H_2O$. When $Bi(OH)_3$ is
heated to 100°, it changes into $BiO(OH)$, bismuthyl
hydroxide.

5. Drop some of the nitrate into a large quantity of
cold water. This gives basic nitrate of bismuth (sub-
nitrate), $Bi(OH)_2NO_3$. This basic nitrate when heated
yields the yellow bismuthous oxide $2Bi(OH)_2NO_3 =
Bi_2O_3 + 2H_2O + NO_2 + N_2O_3$.

6. Pass a current of sulphuretted hydrogen through a solution of any bismuth salt. Try the precipitate for solubility in ammonia and in nitric acid. The black precipitate is Bi_2S_3.

7. Try if the sulphide is soluble in potassic sulphide or ammonic sulphide. Compare this with arsenic and antimony.

8. Treat a solution of bismuthyl hydroxide with a solution of bichromate of potash, $K_2Cr_2O_7 + 2BiO(OH) = (BiO)_2Cr_2O_7 + 2KOH$.

9. Dissolve some bismuth in aqua regia. Dissolve some of the trioxide in hydrochloric acid. In each case there is formed bismuth trichloride, $BiCl_3$, which may be obtained by evaporation. When the solution of the trichloride is thrown into excess of water an insoluble white precipitate is formed, having the composition BiOCl, oxychloride of bismuth or bismuthyl chloride.

10. Add a solution of the nitrate to solution of an alkaline carbonate,

$$2Bi(NO_3)_3 + 3K_2CO_3 = (BiO)_2CO_3 + 6KNO_3 + 2CO_2.$$

18.—Notes on Bismuth.

Bismuth is the distinctly metallic element of the nitrogen group. Its chief compounds are similar in form to those of the other elements, but it does not unite with hydrogen, and its trioxide is not acidic, while the pentoxide is only weakly so.

The most important compound of bismuth is the nitrate, which is theoretically interesting because of its

forming the basic salt by one or two hydroxyl groups displacing an equal number of acid radicals, thus,

$$\text{Bi} \begin{cases} NO_3 \\ NO_3 + H_2O = \text{Bi} \begin{cases} NO_3 \\ NO_3 + HNO_3 \\ HO \end{cases} \\ NO_3 \end{cases}$$

$$\text{or Bi} \begin{cases} NO_3 \\ NO_3 + 2H_2O = \text{Bi} \begin{cases} NO_3 \\ HO + 2HNO_3 \\ HO \end{cases} \\ NO_3 \end{cases}$$
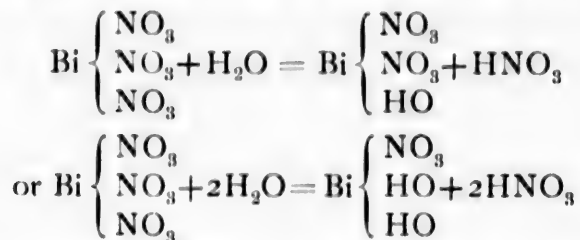
Definition.—A basic salt is one in which the acid part of a molecule does not completely saturate the basic part.

Nitrate of bismuth in solution with an alkaline hydrate yields a white powder, $Bi(OH)_3$. On heating, this successively changes into $BiO(OH)$ and Bi_2O_3. This oxide when dissolved in nitric acid yields $Bi(NO_3)_3$ again ; and when treated with chlorine and potassic hydrate forms $HBiO_3$, a red powder. The acid when heated changes first into Bi_2O_5, then into Bi_2O_4. With an alkaline carbonate, the nitrate forms what is commonly called carbonate of bismuth, but what is in reality bismuthyl carbonate, $(BiO)_2CO_3$.

19.—Questions and Exercises.

1. Boil some arsenic trioxide in the solution of an alkaline carbonate, K_2CO_3 for example ; divide into two parts, to one add some copper sulphate solution and a few drops of ammonia ; to the other some silver nitrate solution with ammonia. The former yields Scheele's green, $CuHAsO_3$, cupric hydric arsenite ; the latter arsenite of silver, Ag_3AsO_3.

$$As_2O_3 + 2K_2CO_3 + H_2O = 2K_2HAsO_3 + 2CO_2$$
$$K_2HAsO_3 + CuSO_4 = CuHAsO_3 + K_2SO_4.$$
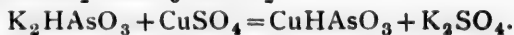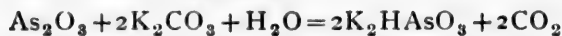
Write the reaction for the silver salt.

2. Prepare a solution of arsenious acid, by boiling arsenic trioxide in water. Divide it into two parts, through one pass a current of chlorine, into the other drop some powdered iodine. Test both with nitrate of silver. Write equations.

3. To a solution of arsenic acid, add some sulphurous acid, or pass a current of sulphur dioxide through it ; boil, to expel the sulphur gas, then test with silver nitrate solution.

4. Try if fusing together arsenious oxide and a nitrate will give arsenic acid.

5. To a solution of an antimony salt, add hydrogen sulphide, heat the precipitate with hydrochloric acid, dilute the solution largely.

6. Construct a table to show whether the elements of the nitrogen group change directly or inversely with the increase of atomic weights in the following particulars :—

(1) State of rigidity at ordinary temperatures, (2) melting points,

$$N - ; \quad P, 45° ; \quad As, 600? ; \quad Sb\ 450° ; \quad Bi, 270.$$

(3) Metallic appearance, (4) specific gravity, $N = .97$, air $= 1$,

$$P\ 1.9, \text{water} = 1 ; \quad As, 5.7 ; \quad Sb, 6.7 ; \quad Bi, 10.$$

(5) Basicity of oxides, (6) colour of the sulphide precipitated by H_2S.

7. Do the conditions favour the formation of arsine, when a hydrochloric acid solution of arsenic is being decomposed by electrolysis?

8. A current of chlorine is passed into solutions of ammonia, arsine and stibine. What will take place in each case?

9. Some arsenical pyrites is roasted in an open tube, the white substance that collects on the cold part of the tube is scraped off and divided into two parts, one part is boiled with water, the other with nitric acid. After cooling, both solutions are tested with silver nitrate. Chlorine is then passed through the aqueous solution and sulphur dioxide gas through the other. After standing for some time, they are again tested with silver nitrate. Trace the changes, giving equations.

7

10. Write formulæ for the following compounds : —disodic phosphate, ammonium metaphosphate (neutral), dipotassic hydric sulphantimoniate, antimonyl potassic tartrate ($\overline{T} = H_2 C_4 H_4 O_6$).

11. (NO)Cl is nitrosyl chloride, (NO$_2$)Cl is nitroxyl chloride, (PO)Cl$_3$ is phosphoryl chloride, (SbO)Cl is antimonyl chloride, (BiO)Cl is bismuthyl chloride. Write graphic formulæ for each which will satisfy the valencies of the elements whose symbols stand first in each group.

12. A piece of phosphorus is acted on by strong nitric acid ; another piece is lowered into a vessel of chlorine and after a time water is added ; a third piece is placed in aqua regia (see High School Chemistry). What will be the reactions in each case ? Give equations.

20.—Notes on the Nitrogen Group.

The members all have the valencies three and five. Nitrogen and phosphorus are non-metallic both in physical and chemical properties, arsenic is somewhat metallic in appearance, but its oxides are acidic. Antimony is distinctly metallic in appearance, and while its oxides are generally acid forming, they are less strongly so than those of arsenic, and the trioxide acts as a base with strong acids, thus,—Sb(NO$_3$)$_3$ is antimony nitrate and SbONO$_3$ antimonyl nitrate. Bismuth is still more metallic than antimony ; the trioxide is basic, and the pentoxide is feebly acidic, forming salts with strong bases, such as the alkalies.

All except bismuth form hydrides having the composition XH$_3$; these are soluble in water.

All except arsenic form oxychlorides from the interaction of the chlorides and water. All except arsenic form monad radicals of the composition MO.

The following is a tabular statement of the oxides and oxyacids of the members of this group :—

	OXIDE.	ACID.
Nitrogen....	N_2O	HNO
	$NO = N_2O_2$	———
	$N_2O_3 - (N_4O_6)$	HNO_2
	$NO_2 = (N_2O_4)$	
	N_2O_5	HNO_3 corresponds to the meta-acids of other members.
Phosphorus .	P_4O	———
	———	H_3PO_2
	P_4O_6	H_3PO_3
	P_2O_4	$H_4P_2O_6$
	P_2O_5	H_3PO_4, at 200° $H_4P_2O_7$, at 400° HPO_3
Arsenic ...	As_4O_6	H_3AsO_3, known by its salts.
	As_2O_4	———
	As_2O_5	H_3AsO_4, $H_4As_2O_7$, $HAsO_3$.
Antimony	Sb_4O_6	H_3SbO_3 (oxide both basic and acidic).
	Sb_2O_4	———
	Sb_2O_5	H_3SbO_4, $H_4Sb_2O_7$, $HSbO_3$.
Bismuth ...	Bi_2O_2	
	Bi_2O_3	
	Bi_2O_4	
	Bi_2O_5	$HBiO_3$, $H_4Bi_2O_7$ (from its salts).

Among the oxides of nitrogen N_2O when heated readily breaks up and acts as an oxidizer, NO with oxygen changes spontaneously into NO_2 and N_2O_3, while, on the other hand, these higher oxides are readily reduced to NO, and act as oxidizing agents. The oxides that are anhydrides form acids by dissolving in water.

In the case of oxides of phosphorus, the compound formed depends on the masses taking part in the chemical action. P_2O_3 heated in presence of oxygen burns to P_2O_5.

Both are anhydrides.

When arsenic and antimony are burned in air they oxidize to the *ous-* oxide only, and this does not combine with more oxygen.   To form the pentoxide, the lower oxide is treated with some strong oxidizing agent, such as chlorine or nitric acid.   A similar statement applies to bismuth.

All the hydrides are oxidizable through the action of heat, both elements uniting with oxygen in each case, hence all are reducing agents.

All the elements form sulphides of the same type as the *ous* and *ic* oxides, simply changing oxygen for sulphur.   All form sulphides, and antimony and bismuth form sulphates and nitrates.

CHAPTER X.

SULPHUR GROUP.

Oxygen, Sulphur, Selenium, Tellurium.   Only the first two are to be considered.

1.—Notes on Oxygen.

Preparation.— Oxygen may be obtained by three general methods.

(*a*) By electrolysis of oxides or hydrates. For this purpose the compound must be liquefied by fusion, if it is solid at ordinary temperatures.

(*b*) By the decomposition of oxygen compounds by heat. Those more commonly employed for this purpose are chlorates, nitrates, chromates, peroxides, and, in rare cases, simple oxides.

(*c*) By displacement, as in the case of sulphuric acid and manganese dioxide, chlorine and water, fluorine and water.

Compounds.—The simple compound formed by the union of oxygen with an element is called an oxide. Oxygen thus unites with all elements so far as known, except fluorine and bromine. When the oxygen of an oxide is replaced by hydroxyl, HO, an hydroxide or hydrate is formed. It sometimes happens that an element of well-defined valency unites with oxygen in a proportion greater than that required by the valency of the element, thus H_2O_2, PbO_2, Na_2O_2 are examples. Such compounds are called **peroxides**, because with acids they do not form salts of the type of the oxide and water; but oxygen is freed, and the salts corresponding to the lower oxide are produced; thus,—$2Na_2O_2 + 4HCl = 4NaCl + O_2 + 2H_2O$.

The peroxides are, in general, somewhat unstable, parting readily with oxygen, hence their value as oxidizing agents.

The oxides are sometimes classed as *basic, acidic* and *peroxides*. Basic oxides form hydrates with water and neutralize acids to produce salts. Acidic oxides, in union

with water, make acids. Peroxides do not neutralize acids, though they may form hydrates with water. This division is not a satisfactory one because they over-lap one another, frequently the same oxide being both acidic and basic, depending on the other substance taking part in the action. The other chief compounds of oxygen are the oxyacids and their salts. Some of these, such as the nitrates, chlorates and permanganates, are easily decomposable and yield free oxygen, but most of the compounds are not readily broken up in that way.

Ozone.—This allotropic form of oxygen is supposed to be due to a different atomic arrangement of the molecule from that in free oxygen. The symbol O_3 expresses the supposed fact that the molecule is triatomic. The alteration in volume when oxygen is changed into ozone or *vice versa* is in accord with this hypothesis. Any divalent gaseous element freed from its combinations might take on an allotropic form due to a similar grouping, but with monad elements it is not theoretically possible.

2.—Notes on Sulphur.

Preparation.—Besides the sulphur which is found native, this element is separated in many chemical reactions, such as by the decomposition of hydrogen sulphide either in presence of oxygen, chlorine or sulphur-dioxide, thus,—

$$2H_2S + 2H_2O + O_2 = 4H_2O + 2S$$
$$H_2S + Cl_2 = 2HCl + 2S$$
$$SO_2 + 2H_2S = 2H_2O + 3S$$
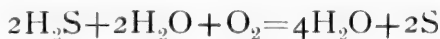
by the breaking down of the polysulphides of alkali metals by acids, see page 27, and by the decomposition of thio-sulphates, thus,—

$$K_2S_2O_3 + H_2SO_4 = K_2SO_4 + H_2O + SO_2 + S.$$

(See H. S. Chem., p. 180.) This is the basis of one method for the recovery of the sulphur in the alkali waste of the soda works. (See under sodium.) The calcium sulphide is changed to thio-sulphate by blowing air through it, then with hydrochloric acid it is decomposed, thus,—

$$CaS_2O_3 + 2HCl = CaCl_2 + H_2O + 2S.$$
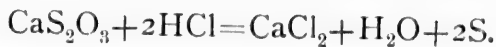
Like the oxides, many sulphides and polysulphides are decomposed by heat, but frequently the sulphur at high temperature unites with oxygen to form SO_2.

Properties.—Sulphur, in its combinations, very much resembles oxygen. It also is known in a number of allotropic forms, which are probably due to various atomic groupings in the molecules. The well-known modifications in the fusing and suddenly cooling of ordinary sulphur can be easily observed by very gradually melting sulphur in a tube or dish, stirring it from time to time and dropping a little of it into cold water. The vapour density of sulphur also indicates that the molecule up to a temperature of 500 C. is hexatomic, that above this temperature the molecules begin to break down into diatomic ones, and at 1000° this decomposition is complete, $S_6 = 3S_2$. This would seem to indicate that the atoms composing the molecule are arranged in groups, and that the increased kinetic energy causes the attachment between the groups to be broken.

3.—Compounds of Sulphur.

Sulphur and hydrogen,

$$\left.\begin{array}{l} ZnO+2HCl=ZnCl_2+H_2O \\ FeS+H_2SO_4=FeSO_4+H_2S \end{array}\right\}A \quad \left.\begin{array}{l} 2H+O=H_2O \\ 2H+S=H_2S \end{array}\right\}C$$

$$\left.\begin{array}{l} Na_2O_2+2HCl=2NaCl+H_2O_2 \\ K_2S_5+2HCl=2KCl+H_2S_2+3S \end{array}\right\}B$$
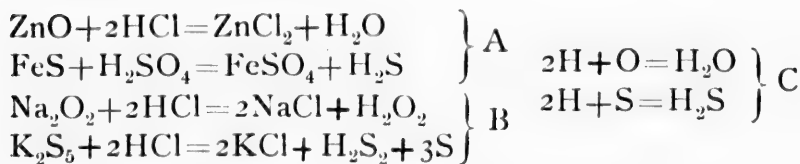
The equations A and B show the similarity of the methods by which oxides of hydrogen and the sulphides of hydrogen are obtained. When hydrogen is ignited in oxygen gas the oxide is produced, but when the ignition occurs in sulphur vapour the sulphide is formed, as in C.

The sulphide is easily decomposed, as when the gas is passed through a red hot tube, or ignited, or passed into a solution of most metallic salts, or in presence of a halogen. When the gas is ignited, if the supply of air be limited, the hydrogen burns, but part, at least, of the sulphur remains unconsumed, as a deposit on the vessel.

The persulphide is of somewhat doubtful composition, and as prepared from potassium pentasulphide, contains free sulphur. It is mentioned here simply for comparison with the oxide.

4.—Oxides of Sulphur.

These are the dioxide, SO_2, the trioxide, SO_3 the sesquioxide, S_2O_3, and heptoxide S_2O_7. All may be produced by union of the elements. Sulphur ignited in oxygen forms SO_2. SO_2 heated with oxygen over a platinum sponge gives SO_3. SO_3 cannot be obtained by burning

sulphur in air, because the trioxide, at a temperature below that of burning sulphur, breaks down into the dioxide and oxygen. SO_3 fused with sulphur produces S_2O_3.

S_2O_7 is formed when electric sparks pass through sulphur dioxide and oxygen. The oxides are mostly prepared, however, by reducing higher compounds. The dioxide and trioxide alone are important. The former is obtained by the reduction of sulphuric acid by the nascent hydrogen formed when a metal acts on part of the acid, thus : $Cu + H_2SO_4 = CuSO_4 + 2H$

and $\qquad 2H + H_2SO_4 = 2H_2O + SO_2.$

Hydrogen sulphide acts similarly, $H_2S + H_2SO_4 = 2H_2O + SO_2 + S.$

5.—Acids of Sulphur.

Hydrogen sulphide shows acid properties. Its hydrogen is replaceable by metals, hence the formation of metallic sulphides and hydrosulphides, as CuS and KHS.

Oxyacids.—The two most important of these are obtained by dissolving the dioxide and trioxide in water. They are sulphurous, H_2SO_3, and sulphuric, H_2SO_4. The preparation of the latter depends on the property that sulphur dioxide possesses of reducing nitrogen tetroxide in presence of water, thus forming sulphur trioxide and nitrogen dioxide.

Sulphuric acid, when boiled, loses water. The hydrated acid having the formula $H_2SO_4 + 4H_2O$ has been separated ; but, by heating, it parts with successive portions of water, as indicated by the formulæ $H_2SO_4 +$

$3H_2O$, $H_2SO_4+2H_2O$, $H_2SO_4+H_2O$, H_2SO_4, $H_2S_2O_7=$ $2H_2SO_4-H_2O$. Phosphoric anhydride, P_2O_5, when mixed with sulphuric acid and distilled absorbs water and allows the trioxide to pass over. It is advantageous here, of course, to use acid already largely dehydrated by heat. $H_2SO_4+P_2O_5=2HPO_3+SO_3$.

The method of preparing the commercial acid has already been described (see H. S. Chem., page 183). If sulphur be oxidized to the trioxide, this, with water, will give the acid. The trioxide cannot be produced by heating sulphur, but it may be obtained by (a) oxidizing the dioxide as in the case where nitrogen trioxide is reduced, or when a halogen is dissolved in an aqueous solution of the dioxide, (b) by oxidizing sulphur directly, as when it is boiled with nitric acid, or when it is added to a solution of chlorine in water.

$$S+6HNO_3=SO_3+3H_2O+6NO_2$$

or $$S+4HNO_3=SO_3+2H_2O+N_2O_3+2NO_2$$

$$S+3Cl_2+3H_2O=SO_3+6HCl.$$

It will be remembered that hydrochloric acid is prepared by heating a chloride with sulphuric acid, but with a bromide or iodide, a further reaction occurs by which the halide acid acts on the sulphuric acid and decomposes it, at the same time depositing the bromine or iodine. Water is also formed, along with sulphur dioxide, free sulphur or hydrogen sulphide, depending on the quantity of the halide acid present. Probably all three reactions generally go on together. A similar decomposition occurs with hydrogen sulphide. A piece of zinc dropped

into hot concentrated sulphuric acid brings about such reactions as the following,—

$$5Zn + 5H_2SO_4 = 5ZnSO_4 + 10H$$
$$2H + 2H_2SO_4 = 2H_2O + H_2S + SO_2$$
$$H_2S + H_2SO_4 = 2H_2O + SO_2 + S.$$
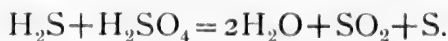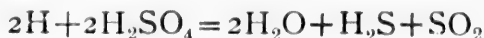
Sulphurous acid H_2SO_3 has not been separated, as it breaks up into its anhydride and water when either evaporated or displaced from its compounds by a stronger acid. Its salts are important.

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6. – Thio-Acids.

Sulphurous acid oxidizes to sulphuric. Similarly, if a salt of sulphurous acid, Na_2SO_3, be boiled with sulphur it becomes $Na_2S_2O_3$, thio-sulphate of sodium,—the sodium salt of thio-sulphuric acid $H_2S_2O_3$. This acid has not been isolated either. In popular language it is hyposulphurous acid and $Na_2S_2O_3$ is hyposulphite of soda, but the names just quoted should belong to H_2SO_2 and Na_2SO_2.

There is a series of the sulpho-acids of sulphur, which may be mentioned here. They are,—

thio-sulphuric acid, $H_2S_2O_3 = SO_2 {<}{\substack{HO \\ HS,}}$ while sulphuric

acid is $SO_2 {<}{\substack{HO \\ HO.}}$

dithionic acid, $H_2S_2O_6$
trithionic acid, $H_2S_3O_6$
tetrathionic acid, $H_2S_4O_6$
pentathionic acid, $H_2S_5O_6$
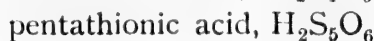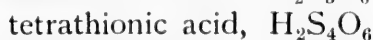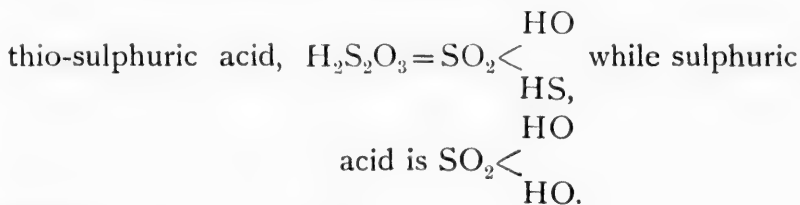
7.—Sulphur and the Halogens.

When dry chlorine is passed over heated sulphur, as powder, sulphur monochloride S_2Cl_2 is formed. By saturating this monochloride with chlorine gas at low temperatures, the dichloride SCl_2 and tetrachloride SCl_4 are obtained. S_2Br_2 and S_2I_2 are also known. It will be noticed that in these lower halide compounds, sulphur has a valency which it does not exhibit in the oxygen compounds; the SCl_4 corresponding in this respect to SO_2.

Just as in the oxygen compounds, one atom of oxygen may be replaced by two hydroxyl groups,— $S \begin{cases} O \\ O \end{cases}$ becoming $S \begin{cases} (OH)_2 \\ O \end{cases} = H_2SO_3$, so the oxygen may give place to chlorine, thus $S \begin{cases} O \\ O \end{cases}$ changes to $S \begin{cases} O \\ Cl_2, \end{cases}$ thionyl chloride. Another somewhat similar compound is sulphuryl chloride, which contains the group SO_2, and may be looked upon as sulphuric acid in which hydroxyl is replaced by chlorine, thus $SO_2 \begin{cases} HO \\ HO \end{cases}$ by substitution becomes $SO_2 \begin{cases} Cl \\ Cl \end{cases} = SO_2Cl_2$ sulphuryl chloride. Naturally, if we have $SO_2(HO)_2$ changing to SO_2Cl_2, one looks for the intermediate compound, when one hydroxyl group is replaced. This compound is also known. It is $SO_2 \begin{cases} OH \\ Cl \end{cases} = SO_2(OH)Cl$, chlorsulphuric acid.

CHAPTER XI.

THE IRON GROUP.

I.

The elements resembling one another sufficiently to be put in this group are chromium, manganese, iron, nickel, cobalt. Of these only manganese and iron are to be considered here.

Both are greyish white metals, capable of being reduced from their oxides by the action of carbon at high temperatures. Both are fusible and ductile; manganese is much harder than iron though. Both are base forming as well as acid forming elements; in iron, however, the basic properties are much stronger than the acid ones, while in the case of manganese, though the basic properties predominate, they are not so marked as with iron.

These elements, as bases, form two series of compounds,—the -ous compounds in which the metals are bivalent, and the -ic compounds in which they are trivalent. The types of these are MO and M_2O_3.

2.—Iron.

EXPERIMENTS.

A—The Ferrous Compounds.

1. Put some cuttings of iron wire, or some coarse iron filings, into a beaker and cover with dilute hydrochloric acid; keep iron in excess until gas ceases to come off from the liquid when heated nearly to boiling. The

fluid should be bluish green in colour. Fill a well stoppered bottle with this liquid and preserve for future use. The fluid is a solution of ferrous chloride, $FeCl_2$,

$$Fe + 2HCl = FeCl_2 + H_2.$$

2. Set a portion of the solution of ferrous chloride containing some free acid apart for a few days in an open vessel. It changes colour and, by taking up oxygen from the air, becomes ferric chloride, Fe_2Cl_6, thus :—

$$4FeCl_2 + 4HCl + O_2 = 2Fe_2Cl_6 + 2H_2O.$$

3. Pass through ferrous chloride solution a current of chlorine, $2FeCl_2 + Cl_2 = Fe_2Cl_6$.

4. Prepare a strong solution of ferrous chloride, in excess of hydrochloric acid, in a large beaker ; add nitric acid, and heat until the mixture foams up and turns reddish brown. $6FeCl_2 + 2HNO_3 + 6HCl = 3Fe_2Cl_6 + 2NO + 4H_2O$. The foaming at the end of the operation is caused by the escape of nitric oxide gas which is formed but is not held in solution by the ferric chloride. Save this chloride for further experiments.

5. To ferrous chloride add a drop or two of silver nitrate solution. The greenish substance is ferrous nitrate. Can it be prepared by acting on iron wire with nitric acid ?

6. Heat some iron with dilute sulphuric acid, evaporate to dryness. The green salt is ferrous sulphate $FeSO_4$, (copperas).

7. Dissolve some ferrous sulphate, add ammonium hydrate. The precipitate is ferrous hydrate. Try if other alkaline hydroxides will yield the same compound. Try lime water.

8. Pass hydrogen sulphide into a solution of any *ous* salt of iron in presence of free acid. Repeat, but make the solution alkaline.

9. Add a solution of an alkaline carbonate to ferrous chloride. Will the sulphate or the hydrate give similar results? The greenish salt is ferrous carbonate.

B—The Ferric Compounds.

10. To some ferric chloride add iron filings and let the mixture stand, but shake it frequently. Compare the result with ferrous chloride, $Fe_2Cl_6 + Fe = 3FeCl_2$.

11. Try if chlorine or nitric acid will oxidize ferrous sulphate to the ferric compound.

12. In one vessel put some pieces of iron wire with dilute nitric acid ; in another some iron wire with strong nitric acid. The ferric nitrate, $Fe_2(NO_3)_6$ is formed in the first case.

13. Heat strongly on a piece of mica, a crystal of copperas.

14. Prepare some ferric hydrate, $Fe_2(OH)_6$, by treating ferric chloride with ammonium hydrate. Filter out the precipitate, divide it into two parts and ignite one of them strongly on mica. $Fe_2(OH)_6 = Fe_2O_3 + 3H_2O$. Test the hydrate and oxide for solubility in hydrochloric acid.

15. Drop into a solution of potassic ferrocyanide, (yellow cyanide), K_4FeCy_6, some ferric chloride. Prussian blue is formed. Repeat the experiment, but use a ferrous salt. Again repeat both parts, but use ferricyanide, red cyanide, $K_6Fe_2Cy_{12}$.

16. Try if ferric chloride can be reduced by (*a*) passing through it a current of hydrogen, (*b*) generating hydrogen in the solution, by dropping into it, when acidified, some pieces of zinc.

17. Pass a current of hydrogen sulphide into some solution of ferric chloride. The white precipitate is sulphur.

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + 2S.$$
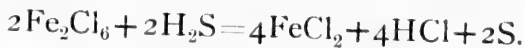
18. Pass a current of sulphur dioxide gas into a solution of ferric chloride.

19. Make a mixture of one part of the finest iron powder and two parts of potassic nitrate. Heat this in a hard glass tube; after becoming red hot let the mass cool, then dissolve it in water. A purple solution of potassic ferrate, K_2FeO_4 should be obtained.

3.—Notes on Iron.

Iron is a greyish white, ductile, malleable, fusible metal. In the form of fine powder, such as results from the reduction of ferric oxide (*ferrum redactum*, or *fer reduit*), it is black.

Occurrence.—The chief ores of iron are magnetite, Fe_3O_4; haematite, Fe_2O_3; limonite, a mixture of ferric oxide and ferric hydroxide; siderite or spathic iron ore, $FeCO_3$; clay ironstone, a spathic ore containing clay and sand.

Preparation.—Iron is obtained from the ores by reducing with carbon. The operation is carried on in blast furnaces that are charged with mixtures of ore, coke and

limestone. The latter forms a fusible slag that partly prevents oxidation of the metal, and partly prevents loss of the iron by carrying off the waste products.

Varieties.—There are three chief varieties of iron,—cast iron, wrought iron and steel. The first of these is the iron as it comes from the furnace. In the extracting process part of the carbon unites with the iron; the amount of this carbon varies from 3.5 to 6 per cent. of the mass. There are generally other impurities present consisting of manganese, sulphur, phosphorus and silicon. The conversion into wrought or malleable iron is brought about by getting rid of these foreign substances, partly by oxidation in furnaces, partly by mechanical means. The amount of carbon remaining is about 0.5 per cent. This form of iron is malleable, ductile, and capable of being welded when hot. Steel contains from one to two per cent. of carbon. It may be prepared by (1) oxidizing the carbon out of cast iron until the required quantity only is left, (2) heating refined iron with charcoal or coke powder. The former, with proper modifications, is the basis of the Bessemer process.

4.—Compounds of Iron.

Oxides.—Iron forms with oxygen three oxides,—ferrous oxide, FeO, ferric oxide, Fe_2O_3, and ferroso-ferric oxide, Fe_3O_4. Ferrous oxide is the black powder obtained when hydrogen is passed over ferric oxide heated to about 300°. Ferric oxide (sesquioxide) is produced by the action of damp air on iron or by igniting ferric hydrate. It is also a common ore of iron, red

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haematite. Ferroso-ferric (magnetic) oxide, is another
frequently occurring ore, magnetite, and is formed when
steam is passed over red hot iron. This oxide is gener-
ally believed to be a combination (not a mixture) of the
ferrous and ferric oxides, thus,—Fe_2O_3FeO. There are
other ferric compounds analogous to this, for example,
Fe_2O_3MgO, Fe_2O_3CaO, Fe_2O_3ZnO. These are the
spinels mentioned under aluminium. They have the
type formula R_2O_3MO, where $R=Cr$, Fe, Al, Ni, or Mn,
and $M=Fe$, Mg, Zn, Mn, or Cr.

Hydrates.— Iron forms two hydroxides, the ferrous and
ferric, when the salts of these respective classes are pre-
cipitated with an alkaline hydrate. The former is a
white precipitate, that oxidizes on exposure to the air.
The latter is a reddish brown precipitate, that yields ferric
oxide when ignited.

Ferric Acid.—H_2FeO_4 has not been separated, but the
potassium sodium, and barium salts of it are known,
K_2FeO_4, Na_2FeO_4 and $BaFeO_4$. (See ex. 20.)

Chlorides.—Both the ferrous and ferric chlorides are
easily prepared, the former, in solution as a bluish green
liquid, by the action of dilute hydrochloric acid on iron ;
the latter as a yellow or reddish compound formed by
the action of oxidizing agents, such as chlorine or nitric
acid on the ferrous chloride, or by passing chlorine over
hot finely divided iron. This latter process may be
reversed, and by means of reducing agents, such as
sulphurous acid and nascent hydrogen, the ferric salt
may be changed to the ferrous. (Compare arsenic and
antimony.)

Sulphates.—The ferrous sulphate, $FeSO_4 + nH_2O$ is

formed when iron in excess is dissolved in sulphuric acid. The quantity of water of crystallization taken up on evaporation depends on temperature and presence of air. The highest value of n is 7, but in some cases 5 molecules are present, in others 4, again 1 ; and by proper treatment the anhydrous salt may be obtained. The sulphate is insoluble in sulphuric acid and in absolute alcohol. This salt is formed in nature by the action of damp air on pyrites, FeS_2.

Ferric sulphate is obtained by oxidation of the ferrous salt, or by dissolving ferric hydroxide or oxide in sulphuric acid. Both sulphates form double salts with the alkalies, thus $Fe(Na)_2(SO_4)_2 + 6H_2O$ and $FeNa(SO_4)_2 + 12H_2O$. The latter series (ferric) form the iron alums.

Sulphides.—The ferrous sulphide is obtained either by roasting together iron and sulphur, or by the action of hydrogen sulphide on an alkaline solution of a ferrous salt. From a ferric salt the hydrogen sulphide precipitates the ferrous sulphide and sulphur.

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl$$
$$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$
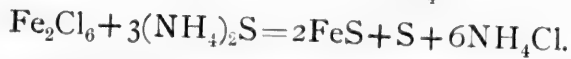
Ferric sulphide Fe_2S_3 is an unimportant compound.

Iron disulphide FeS_2 is iron pyrites, a very common constituent of rocks. When heated to redness it is reduced to the monosulphide.

Arsenical pyrites, mispickel, is a sulphide of iron and arsenic, $FeAsS$.

Cyanides.—Carbon in combination with nitrogen forms cyanogen, CN, (Cy). The acid of this is HCN, hydro-

cyanic acid. There are two double cyanides of iron and potassium. Ferrocyanide, K_4FeCy_6 and ferricyanide $K_3FeCy_6 = K_6Fe_2Cy_{12}$. The former is a yellow crystalline solid, the latter is red, (respectively yellow and red prussiate of potash). With a ferric salt the ferrocyanide yields Prussian blue. With a ferrous salt, the ferricyanide yields Turnbull's blue (light coloured).

5.—Tests.

(A)—Ferrous Compounds.

(1) Alkaline hydrates precipitate $Fe(OH)_2$, which soon changes from white or grey to reddish brown, $Fe_2(OH)_6$.

(2) Alkaline carbonates precipitate ferrous carbonate $FeCO_3$, white or grey in colour, changing to brown $Fe_3(OH)_6$.

(3) Ammonium sulphide precipitates black sulphide of iron, FeS ; hydric sulphide does not, except in alkaline solutions.

(4) Ferricyanide precipitates a dark blue solid, insoluble in acids but decomposed by alkalies.

(B)—Ferric Compounds.

(1) Alkaline hydrates precipitate ferric hydroxide $Fe_3(OH)_6$.

(2) Alkaline carbonates also precipitate the hydroxide.

(3) Hydrogen sulphide reduces the ferric solutions to ferrous with the precipitation of free sulphur.

(4) Ammonium sulphide reduces the ferric solution to ferrous and deposits free sulphur, but at the same time throws down the ferrous sulphide as a black precipitate.

(5) Ferrocyanide precipitates Prussian blue, insoluble in acids, but decomposed by alkalies.

(6) Sulphocyanides, for example KCNS, give blood red colour to ferric solutions, but not to ferrous.

Ferrous compounds and their solutions are generally green in colour.

Ferric compounds and their solutions are reddish, yellow or brown.

6.—Manganese.

EXPERIMENTS.

Manganous compounds, type $MnCl_2$.

1. Manganese dioxide heated with sulphuric acid yields oxygen. When this gas ceases to come off, the solution contains manganese sulphate. Filter and add to the filtrate slowly an alkaline hydrate solution. If a precipitate is thrown down filter again, and evaporate some of the filtrate, which should be pink or reddish in colour. The precipitate with the alkali consists of iron contained as an impurity in the dioxide $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$. Preserve the rest of the filtrate.

2. If the residue from the preparation of chlorine, by the action of hydrochloric acid on manganese dioxide, be filtered, and the iron, if any precipitated, as in ex. 1, the solution will be one of manganous chloride, $MnCl_2$.

3. Add to either the sulphate or the chloride solution some sodium carbonate, $MnSO_4 + K_2CO_3 = MnCO_3 + K_2SO_4$. The carbonate is at first white, but soon becomes dark coloured by oxidation.

4. Repeat the last experiment, but use caustic soda instead of the carbonate. $MnSO_4 + 2Na(OH) = Na_2SO_4 + Mn(OH)_2$. This also oxidizes, thus,—$2Mn(OH)_2 + O_2 = Mn_2O_2(OH)_2$.

5. Add ammonium sulphide to manganous sulphate solution, reddish manganous sulphide is formed.

Manganic compounds, type Mn_2Cl_6.

6. Melt on a piece of mica, or in a small iron vessel, some solid caustic potash, stir into this, when fused, a mixture of manganese dioxide with a little powdered chlorate of potash. When heated to redness, the mixture should turn green in colour.

$$3KOH + KClO_3 + MnO_2 = K_2MnO_4 + KCl + O_2 + H_2O.$$

K_2MnO_4 is potassic manganate, the potassium salt of manganic acid, H_2MnO_4, which has not been isolated. Compare ferric acid.

7. Repeat the last experiment, but use sodium carbonate, manganese dioxide and potassic nitrate.

8. Dissolve some of the green substance and heat it to boiling. Let the liquid then stand for a day. The red liquid is solution of $KMnO_4$, permanganate of potash; and the powder is manganese dioxide.

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

7.—Notes on Manganese.

Manganese is a grey metal, like cast iron, very hard, and oxidizes spontaneously in the air. It is fusible, and soluble in acids. It is prepared from the oxide MnO_2 by a process of reduction similar in principle to that employed in the case of iron.

Occurrence.—The chief compounds of manganese found in nature are the black oxide or pyrolusite, MnO_2; braunite, Mn_2O_3; hausmannite, Mn_3O_4; and manganese spar, $MnCO_3$.

Compounds.

Oxides.—Manganese forms the following compounds with oxygen : Manganous oxide MnO, manganic oxide Mn_2O_3, mangano-manganic oxide, $Mn_3O_4 = MnOMn_2O_3$, manganese dioxide or peroxide MnO_2, and manganese heptoxide Mn_2O_7. Of these Mn_2O_3 and Mn_2O_7 are respectively the anhydrides of manganic and permanganic acids. These oxides connect manganese, on the one hand, with chlorine by the similarity of the heptoxides and the per——ic acids ; and, on the other hand, with lead which has an almost analogous series of oxides, PbO, Pb_2O_3, Pb_3O_4 and PbO_2. When treated with hydrochloric acid the actions with lead oxides, too, are similar to those with the oxides of manganese. There is, however, no Pb_2O_7 known.

Manganous oxide, MnO, is prepared from any of the higher oxides by reducing them in a current of hydrogen (compare iron).

Permanganates.—Of these, the most common is potassium permanganate, formed by acting on potassium or sodium manganate in some way to remove one atom of

the alkaline metal. This may be done as indicated in ex. 9, or by passing a current of carbon dioxide into the manganate solution.

Potassium permanganate is a most useful oxidizing agent on account of the readiness with which it yields up oxygen and becomes reduced to the manganous salt.

Ferrous chloride, for instance, will decolorize a solution of the permanganate, and at the same time become oxidized to ferric chloride. The uses of the permanganate as a test for the purity of water, and as a disinfectant are dependent on this property. The organic substances in the water deoxidize the salt, thus destroying its characteristic colour, and noxious germs are similarly oxidized and burned up by it. A piece of soft paper dipped in the solution of permanganate will soon turn brown, owing to oxidation of the organic ingredients. The following are some examples of this reduction :— $2KMnO_4 + 2FeCl_2 + 8HCl = 2MnCl_2 + 2KCl + 8H_2O + Fe_2Cl_6$

$4KMnO_4 + 4FeSO_4 + 8H_2SO_4 = 4MnSO_4 + 2K_2SO_4 + 2Fe_2(SO_4)_3 + 4H_2O.$

As a disinfectant, its action may be illustrated by the equation, $4KMnO_4 + 6H_2SO_4 = 4MnSO_4 + 2K_2SO_4 + 6H_2O + 5O_2$. The oxygen is, of course, nascent, and the large number of atoms set free from each molecule probably explains their grouping to form ozone, as well as oxygen in the molecular condition.

The permanganic acid may be obtained in solution by treating the barium salt with sulphuric acid.

$$BaMnO_4 + H_2SO_4 = BaSO_4 + H_2MnO_4.$$
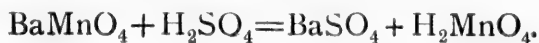
When the permanganate of potash is dropped into a concentrated solution of a caustic alkali and warmed it is reduced to the manganate, $4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2$. After the solution becomes quite clearly green, if it be poured into excess of water it decomposes, as in ex. 8. So long as the alkali is strong the decomposition of the manganate does not occur.

Other Compounds.

Manganous chloride, $MnCl_2$, is obtained by the action of hydrochloric acid on any of the oxides, as in preparation of chlorine.

Manganous sulphide is formed in alkaline solutions by hydrogen sulphide. It is characteristically pink coloured, as are many of the manganous compounds.

The hydrates.—As in the case of most other heavy metals the hydrates are formed by treating the soluble salts with soluble hydroxides. The two most important ones are $Mn(OH)_2$, manganous hydroxide and $Mn_2(OH)_6$ the manganic hydroxide.

Manganous sulphate is formed by the action of concentrated sulphuric acid on manganese dioxide. The ordinary experiment for the preparation of oxygen from these substances leaves as a residue a solution of the sulphate which may be filtered out and purified by precipitating the iron with calcic carbonate.

8.—Tests.

(1) Alkaline hydrates precipitate a white hydroxide that soon turns brown.

(2) A manganous salt boiled with nitric acid and lead dioxide gives red permanganic acid.

(3) Any salt of manganese ignited with caustic potash and a little chlorate of potash gives a bright green mass.

––––––

9.—Questions and Exercises.

1. Pass a current of hydrogen over red hot manganese dioxide in a hard glass tube.

2. Pass a current of carbon dioxide over hot iron filings. Test the escaping gas for carbon monoxide.

3. Boil a little ferrous chloride with some hydrochloric acid, and drop in a crystal of chlorate of potash.

4. Drop into some ferric chloride solution a little sulphuric acid and a piece of zinc. After a time test for a ferrous salt.

5. Mix with a purple solution of permanganate of potash a newly made solution of sulphur dioxide.

6. Pass a current of carbon dioxide into a green solution of manganate of potash.

7. Add a little barium dioxide to an acidulated solution of permanganate of potash. $BaO_2 + 2HCl = BaCl_2 + H_2O_2$ and

$$5H_2O_2 + 6HCl + 2KMnO_4 = 2MnCl_2 + 2KCl + 8H_2O + 5O_2.$$
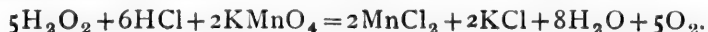
CHAPTER XII.

CALCULATION OF ATOMIC WEIGHTS.

There are several methods used in the determination of atomic weights; the particular ones to be applied in any case depend on the physical and chemical properties of the element. These ways may be briefly summed up as follows :—

(*a*) By determining the masses of equal volumes of elements in the gaseous state and under like conditions of temperature and pressure. This cannot be relied upon for accuracy.

(*b*) By determining the proportions by weight in which elements replace one another. This is valuable, because with proper precautions it gives reliable results.

(*c*) By determining the proportions in which the element whose atomic weight is being found unites with a large number of other elements. For example, carbon in the following compounds yields from

Carbonic oxide	12 of C and	16 of O.
Carbon dioxide	12 of C "	32 of O.
Carbon tetrachloride	12 of C "	142 of Cl.
Methane	12 of C "	4 of H.
Carbon disulphide	12 of C "	64 of S.
Alcohol	24 of C "	22 of other elements.

The smallest proportion by weight in which carbon enters into these combinations is 12, hence the smallest

part by weight in a molecule is 12 times the weight of an atom of hydrogen. It does not follow from this that the atomic weight is 12, because there is no evidence that there is only one atom of carbon in any of these molecules, but it does follow that the atomic weight cannot exceed 12. By comparing as many compounds as possible, it is probable that the atomic weight will be the least found in any compound.

(*d*) By Dulong and Petit's law. This applies only to solid elements. Atomic heat (6.4) divided by specific heat gives atomic weight.

(*e*) By the principle of isomorphism. This is of use only as a check, and not a very reliable one, upon other methods.

(*f*) By comparing analogous elements and their positions in the tabulated lists of the periodic law.

(*g*) By the spark spectrum of the substance (De Boisbaudrun).

(*h*) By the observed lowering of the freezing point of a solvent in which a weighed portion of the element is dissolved (Raoult's method).

These last two methods are scarcely suited for description in a book of this kind, hence are only alluded to in order to complete the list.

CHAPTER XIII.

PERIODIC LAW.

1.

When the elements are written in the order of their atomic weights they fall into certain regular groups, such that those in the same group are closely related to one another in their properties and in the character of their combinations; but are sharply separated from those of neighbouring groups.

For convenience these groups may be written as in Table I.

2

The elements as now arranged consist of two periods of seven each, two others, almost complete, of seventeen each, and three more of the larger groups, but with a considerable number of omissions.

The larger groups each consist of three parts, one of seven elements at the beginning, one of seven at the end and a connection of three elements joining these.

The elements composing these sub-groups are closely related to each other. In Table II. these symbols are rearranged so as to bring the sub-groups together.

This arrangement is generally quoted as Mendelejeff's Table I. In it the elements most nearly related fall into the groups in the vertical columns.

TABLE I.*

(Periods extend across both pages.)

1ST PERIOD — Li 7,	B 9,	B 11,	C 12,	N 14,	O 16,	F 19	
2ND PERIOD — Na 23,	Mg 24,	Al 27,	Si 28,	P 31,	S 32,	Cl 35.5	
3RD PERIOD — K 39,	Ca 40,	Sc 44,	Ti 48,	V 51,	Cr 52,	Mn 55	Fe 56
4TH PERIOD — Rb 85,	Sr 87,	Y 89,	Zr 90,	Nb 94,	Mo 96,	— 100	Ru 104
5TH PERIOD — Cs 133,	Ba 137,	La 139,	Ce 140,	Di 142,	—	—	—
6TH PERIOD —	—	Yb 173,	—	Ta 182,	W 184,	—	Os 191,
7TH PERIOD —	—	—	Th 232,	—	Ur 240,	—	

* It is quite likely that further research will cause a few of the rarer elements, such as La, Er, Yb, and Di to be changed slightly from their present positions, but as the object here is simply to explain the tables, they are given as usually printed.

Fe 56		Co 58,	Ni 58	Cu 63,	Zn 65,	Ga 70,	Ge 72,	As 75,	Se 79,	Br 80
Ru 104		Rh 104,	Pd 106	Ag 108,	Cd 112,	In 113,	Sn 117,	Sb 120	Te 126,	I 127
—			—	—	—	—	Er 166,	—	—	—
Os 191,		Ir 192.5,	Pt 194	Au 197,	Hg 202,	Tl 204,	Pb 206,	Bi 210,	—	—

ements,
, but as

TABLE II.

	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	VIII.		
Hydrides.				MH_4	MH_3	MH_2	MH			
Highest Oxides.	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7			
1st Series........	H 1									
2nd Series (odd).	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19			
3rd Series (odd).	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5			
4th Series (even)	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 58	Ni 58
5th Series (odd)	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80			
6th Series (even)	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100	Ru 104	Rh 104	Pd 106
7th Series (odd).	Ag 108	Cd 112	In 113	Sn 117	Sb 120	Te 126	I 127			
8th Series (even)	Cs 133	Ba 137	La 139	Ce 140	Di 142	—	—	—	—	—
9th series (odd).	—	—	—	Er 166	—	—	—	—	—	—
10th Series (even)	—	—	Yb 173	—	Ta 182	W 183	—	Os 191	Ir 192.5	Pt 194
11th Series (odd)	Au 197	Hg 200	Tl 204	Pb 206	Bi 210	—	—	—	—	—
				Th 232		Ur 240				

3.

The following table is another arrangement which shows the relationship of the groups of elements in a somewhat better way, because of the positions in the schedule. Hydrogen is omitted because it is the only representative of its series.

TABLE III.

	1	2	3	4	5	6	7	
I.			K	Rb	Cs			Even Series
II.			Ca	Sr	Ba			
III.			Sc	Y	La	Yb		
IV.			Ti	Zr	Ce	—	Th	
V.			V	Nb	Di	Ta		
VI.			Cr	Mo	—	W	U	
VII.			Mn	Ru	—	Os		
VIII.			Fe / Co / Ni	Rh / Pd	—	Ir / Pt		
I.	Li	Na	Cu	Ag	—	Au		Odd Series
II.	Be	Mg	Zn	Cd	—	Hg		
III.	B	Al	Ga	In	—	Tl		
IV.	C	Si	Ge	Sn	—	Pb		
V.	N	P	As	Sb	—	Bi		
VI.	O	S	Se	Te	—	—		
VII.	F	Cl	Br	I	—	—		

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4.—Comparison of Properties.

Here the vertical columns show the periods (horizontal rows included between the lines) of Table II.

The two rows having the same Roman numeral make up one of Mendelejeff's groups (vertical columns) in Table II.

In the table (III.) the following are important points to be observed: From element to element within each period (vertical column) there is but slight change of properties, yet from the first element to the last one in the period there is all the change from a strong basic to a strong acidic substance. The first element of each period is an alkali, the last is a halogen. The last element in any period differs entirely in its properties from the first of the next. The sub-groups of the large periods begin in the even series with strong basic elements, and end with others that are both basic and acidic (Mn, etc.); while in the odd series the first elements are ordinary metallic bases, and the last ones strongly acid forming. On account of the relationship existing between the members of the groups (horizontal rows) and the small differences between adjoining members of the periods, it might be expected that groups of similar elements would be found together. That this is really the case is shown by the heavy metals being enclosed in the lower dotted space, while in the upper one is a group of metals all rare, occurring together, and very much alike in properties. Immediately adjoining the lower rectangle are some of the light metals, and metallic like elements ; while the other alkaline metals are next the upper rect-

angle. The non-metallic elements are in the triangular space marked off by heavy dots at the lower left hand corner.

The metals connecting the sub-groups of the large periods are intermediate between the strong acid forming and strong base forming elements, as their oxides may be either acidic or basic.

The first period is mostly composed of non-metals, but as periods of higher atomic weight are reached, the metallic elements increase in number.

5.—Valency in the Groups.

In Group I. (in Table III. this is made up of the two horizontal rows numbered I.) the elements are all monads, and conversely all the monad elements are found in Group I. Group II. is made up of diads; III. of triads; and in IV. the valency reaches a maximum with the tetrad carbon group. The nitrogen group, V., is triad, VI. is diad, and VII. is monad. The valency is reckoned from unions with hydrogen where such are known, but when hydrogen compounds do not exist, those with the halogens or with well known monad radicals are employed.

The oxides show a regular increase from the first group to the seventh, as well as a passage through a maximum at the fourth group, on account of two series of oxides being formed by the elements of Groups V., VI., and VII. Thus,—

Group I., II., III., IV., V., VI., VII., VIII.,

Oxides M_2O, MO, M_2O_3, MO_2, $\begin{cases} M_2O_5, & MO_3, & M_2O_7, & MO_4, \\ M_2O_3, & MO, & M_2O, & MO. \end{cases}$

The first series of oxides shows the maximum valence of the elements of each group.

6.—Some Numerical Comparisons.

Each element of a series (horizontal row, Table II.) is nearly the arithmetic mean of the ones before and after it. In cases of small groups of three or four closely related elements, the middle one has its atomic weight often very nearly equal to the mean of the other two. By taking the successive groups of three in a series and noticing how much the middle one of each group differs from the mean of the other two, it is possible to very closely approximate the atomic weight of an element in that series, even if it is not known.

The differences between the atomic weights of members in the same groups, but in adjoining periods is nearly constant. The blank in Group VII., period 6, has been filled in with 100, by comparing the atomic weights, of periods 5 and 6, periods 4 and 6, and taking the mean of the weights of adjacent elements in 6th period.

7.—Physical Properties.

The following table gives the numerical values for some of the physical constants of the elements. The numbers in the density and atomic volume columns are from Meyer's Modern Theories of Chemistry.

TABLE IV.

NUMERICAL VALUES OF CONSTANTS OF THE ELEMENTS.

ELEMENT.	ATOMIC WEIGHT.	DENSITY.	AT. VOL.	MELTING POINT. (Absolute temp.)
Li	7.02	.59	11.9	453
Be	9.1	1.64	5.6	1230
B	11.	2.68	4.	very high
C	12	3.3	3.6	not known
N	14.03	——	——	59
O	16	——	——	very low
F	19	——	——	not known
Na	23.04	.97	23.7	369
Mg	24.3	1.74	13.8	1023
Al	27.01	2.56	10.6	1123
Si	28.33	2.49	11.2	very high
P	31.03	2.3	13.5	528 } red 317 } yellow
S	32.06	2.04	15.7	388
Cl	35.46	1.38	25.6	198
K	39.14	.86	45.4	335
Ca	40.08	1.57	25.4	red heat
Sc	44.1	——	——	——
Ti	48.13	——	——	——
V	51.4	5.5	9.3	——
Cr	52.3	6.8	7.7	about 2.50
Mn	55	8.0	6.9	2170
Fe	56.02	7.8	7.2	2080
Co	58.7	8.5	6.9	2070
Ni	58.6	8.8	6.7	1870

TABLE IV—*Continued.*

ELEMENT.	ATOMIC WEIGHT.	DENSITY.	AT. VOL.	MELTING POINT. (Absolute temp.)
Cu	63.4	8.8	7.2	1330
Zn	65.7	7.15	9.1	690
Ga	69.9	5.96	11.7	303
As	75.09	5.67	13.2	773
Se	79	4.6	17.1	490
Br	79.95	2.97	26.9	266
Rb	85.5	1.52	56.1	311
Sr	87.5	2.5	34.9	{ below Ca { above Ba
Y	89	——	——	
Zr	90	4.15	21.7	very high
Nb	94	6.27	15	——
Mo	95.7	8.6	11.1	very high
Ru	101.65	12.26	8.4	2070
Rh	103.0	12.1	8.6	2270
Pd	106.35	11.5	9.2	1775
Ag	107.93	10.5	10.2	1230
Cd	112.1	8.65	12.9	590
In	113.7	7.42	15.3	449
Sn	119.1	7.29	16.1	503
Sb	120.3	6.7	17.9	710
Te	125 (?)	6.25	20.2	728
I	126.85	4.94	25.6	387
Cs	132.9	1.88	70.6	300
Ba	137.00	3.75	36.5	48

TABLE IV—*Continued.*

Element.	Atomic Weight.	Density.	At. Vol.	Melting Point. (Absolute temp.)
La	142.3	6.2	22.9	710
Ce	140.3	6.7	20.9	———
Di	145.0	6.5	22.3	1273
Yb	173	———	———	———
Ta	182.5	10.8	16.9	———
W	184	19.13	9.6	———
Os	191.3	22.48	8.7	2770
Ir	193	22.42	8.6	2220
Pt	194.3	21.50	9.1	2050
Au	197.22	19.3	10.2	1310
Hg	200.2	13.59	14.7	234
Tl	204.2	11.86	18.1	563
Pb	206.93	11.38	18.1	599
Bi	208.10	9.82	21.1	540
Th	232.4	11.1	20.9	———
U	240.0	18.69	12.8	red heat

The numbers expressing the densities of the elements generally pass, with slight exceptions, from a minimum at the beginning of a period through a maximum at its middle, then decrease towards the end. The atomic volume (quotient of atomic weight by density) varies the reverse way, having high values at the beginning and end of the period but a smaller value near the middle.

The melting points vary in a general way, as do the densities.

Other physical properties, which lie outside of the scope of this book, such as ductility, malleability, refraction of light, magnetic properties, conduction of heat and electricity, also vary in a regular way throughout each period.

8.—Chemical Properties.

The valency of the groups has already been alluded to, viz.,—beginning with Group I., the hydrogen valence of the groups increase until IV. (carbon) is reached, then a decrease takes place, ending with the monad halogens in VIII. In addition to the similarity in properties of the groups of seven each in the vertical columns, there is a remarkable sub-grouping into threes, the elements of each small group showing a very close connection, and generally the atomic weights of these differ by a nearly constant quantity. Examples are Li, Na, K ; Ca, Sr, Ba; P, As, Sb ; O, S, Se ; Cl, Br, I.

The general formulæ for the compounds in the various groups are as follows :—

Group I., MR where M is any element in Group I., and R a unit equivalent of an element or radical,

thus, $LiCl$, $Na(OH)$, K_2O, $AgNO_3$ $NaClO_3$.

Group II., MR_2, thus, $MgCl_2$, $Ca(OH)_2$, SrO, $Hg(SO_4)_2$.

Group III., MR_3, thus, Al_2O_3, $B(HO)_3$, BCl_3.

Group IV., MR_2 and MR_4,

thus, CO, CCl_4, SrO_2, $Sr(OH)_4$, PbO, PbO_2.

Group V., MR_3 and MR_5,

thus, PCl_3, PCl_5, $NO_2(OH)$, $Bi(NO_3)_3$, PH_3, $PO(OH)_3$, P_2O_5.

Group VI., MR_4 and MR_6,

thus, SO_2, SO_3, CrO_3, $SO_2(OH)_2$.

Group VII., $MR.$, MR_2, MR_4, MR_7,

ClH, ClO_2, Cl_2O_7, MnO, MnO_2.

Group VIII., MR_2, MR_3, MR_4,

FeO, Fe_2O_3, $PtCl_4$, $NiSO_4$, NiO_2.

The first three groups do not form hydrides, except rarely, as Na_2H, K_2H and possibly LiH.

9.—Applications of the Periodic Law.

Since each element, as placed in the Tables II. and III., resembles the ones both before and after it in the horizontal line, and those above and below it in the vertical one, it is possible to tell its properties pretty accurately from those of the four surrounding it, once its atomic weight is known, for then its position in the table is assured. This arrangement of the elements also serves as a check in determining doubtful atomic weights. It is probable that elements will yet be found to occupy some of the blank spaces in the table, and their properties can be known with a considerable degree of accuracy even before the elements are discovered.

Group V. may be taken to illustrate some of the relationships among the elements comprising it.

(1) The elements pass from gaseous nitrogen through waxy phosphorus, then to brittle solids, ending with metallic bismuth.

(2) The upper members in the group are entirely acid forming. Towards the middle (V. Sb, Nb) tl .xides are both basic and acidic. Farther down they are basic only.

(3) Some members of the group (N, P, As, Sb,) form hydrides of the composition MH_3. Hydrides of about half the elements in the group are unknown. The hydrides are decomposed (into the elements forming them), at high temperatures.

(4) All form compounds with halogens, particularly Cl, having the composition MCl_3 and MCl_5.

(5) All except N burn directly to M_2O_3 and M_2O. In the acid forming elements these are the anhydrides of the -ous and -ic acids respectively.

(6) The acids generally lose one or more molecules of water when heated.

(7) All except N form sulphides, thus, M_2S_5.

(8) The haloid compounds are all decomposed by water to form the haloid acid and the oxide of the element.

If, then, an element were discovered whose atomic weight were about 168, so that it would fall in Group V., 9th series, it would be reasonable to suppose that its compounds would be of the character of those given above.

CHAPTER XIV.

1.—Chemical Action and Energy.

In every chemical action there is more than a mere joining together, separation, or interchange of atoms among the molecules of the substances affected. This may be shown as follows:—

1. Make a strong solution of caustic potash, and measure 50 cc. of it into a beaker. Into another beaker pour 50 cc. of water. Dilute some hydrochloric acid about one-half. Place all the vessels in a tank of water until they reach a common temperature, then pour 50 cc. of the acid into the beaker of water, having previously placed a thermometer in it, and watch for any change of temperature. Repeat the experiment, but use the potash solution instead of the water.

2. Dilute some sulphuric acid, and after it has cooled to the temperature of the surrounding air place in it a thermometer, drop in some bits of zinc, and observe the temperature.

3. Prepare some sodium amalgam and drop it into a beaker containing a little water. Does the temperature change?

4. Make a mixture of sulphuric acid and water, about one tenth acid; place in this, but not in contact with each other, a strip of zinc and another of copper; then pass a wire from one strip to the other outside of the beaker. Does the temperature change?

5. Try if the temperature of water changes while being decomposed by electricity.

These experiments, which are typical chemical actions, make it clear that accompanying the atomic changes of the reaction, there is in each case a developmeut of free energy appearing here, either as a rise of temperature or as electrification. Now the principle of the "Conservation of Energy" has taught us that energy may be transformed but cannot be created ; hence the chemical action means a rearrangement of the energy of the system as well as of its atoms. If there was no development of heat, electrification or any other form of energy, we should have to deal simply with transferrence of matter, but as it is, any explanation which is complete, must take account of the energy either used up or freed in the change.

Those reactions in which energy (generally as heat) is set free are called **exothermic ;** and those in which energy in some form has to be constantly supplied that the action may continue, are known as **endothermic.** In the former, the chemical action may take place spontaneously ; or, as is more generally the case, means must be taken to bring the molecules of the constituents into very close proximity to each other before the action begins. Once the action has begun, however, the energy developed is sufficient to keep it going. In endothermic reactions, there has to be a constant supply of external energy, else the chemical action at once ceases. The union of hydrogen and oxygen to form water is an exothermic combination; while the breaking up of water by making it part of an electric circuit carrying a current is an endothermic decomposition.

It is customary, in chemistry, to treat of this energy

in terms of heat units. (The thermal unit of physics is a calorie, and is that quantity of heat required to raise the temperature of one gram of water through one degree. For convenience this unit is sometimes multiplied by 1000, and is then written Calorie, thus 1 Cal. = 1000 cal.)

2.—Law of Maximum Work.

When two substances by their union set energy free, it always requires the use of a quantity of energy exactly equal to that freed to bring about decomposition into the original substances, provided that particular decomposition is possible. This, of course, is a deduction from the principle of the Conservation of Energy, and it has been experimentally demonstrated as well.

A chemical action which is either spontaneous, or which goes on without a continual application of external energy, results in the formation of substances of a stable character. This may be otherwise expressed as follows: generally exothermic compounds are stable, while endothermic ones are somewhat unstable. This principle has been expressed as a general law, known as the law of **maximum work**, or the law of **maximum heat development**, thus, when two substances unite spontaneously, they form that compound by which the greatest quantity of energy is set free.

3.—Quantitative Heat Results.

By using such a calorimeter as is required for determining the latent heat of the liquidity of water or the
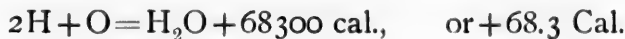
specific heat of a piece of metal, the student can obtain an approximate result for the heat of some common chemical actions.
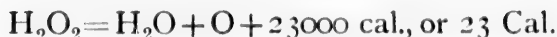
EXPERIMENTS.

1. Weigh out 10 grams of strong sulphuric acid, and dilute it to 100 cc. with water. Then weigh out 5 grams of zinc. After the acid has cooled put it in a glass vessel in a calorimeter (a glass beaker in a box packed with cotton wool will do very well), insert a thermometer and observe the rise of temperature. From this calculate the number of calories freed by 65 grams of zinc when similarly treated.

2. Dissolve 2 grams of solid caustic soda, treat it with an excess of dilute hydrochloric acid, and measure the rise of temperature. Calculate how many calories would be developed from 40 grams of the hydrate.

In order that comparisons may be made between various chemical actions in regard to heat, it has been agreed to take as the unit of the substance a "gram-molecule," that is, that number of grams expressed by the combining weight (atomic weight of elements, and molecular weight of radicals) of the substance. The following are the values in heat units of a few of these reactions:

$$2H + O = H_2O + 68300 \text{ cal.,} \qquad \text{or} + 68.3 \text{ Cal.}$$
$$C + 2O = CO_2 + 97000 \text{ cal.,} \qquad \text{or} + 97 \text{ Cal.}$$
$$H + I = HI - 6000 \text{ cal.,} \qquad \text{or} - 6 \text{ Cal.}$$
$$H + Cl = HCl + 22000 \text{ cal.,} \qquad \text{or} + 22 \text{ Cal.}$$
$$Hg + O = HgO + 30600 \text{ cal.,} \qquad \text{or } 30.6 \text{ Cal.}$$
$$2O_3 = 3O_2 + 72000 \text{ cal.,} \qquad \text{or } 72 \text{ Cal.}$$

$$H_2O_2 = H_2O + O + 23000 \text{ cal., or } 23 \text{ Cal.}$$
$$\text{also} \quad 3O_2 = 2O_3 - 72000 \text{ cal.,} \quad \text{or} -72 \text{ Cal.}$$
$$H_2O + O = H_2O_2 - 23000 \text{ cal.,} \quad \text{or} -23 \text{ Cal.}$$

These symbols mean that when two grams of hydrogen unite with sixteen of oxygen heat enough is set free to raise 68300 grams of water through one degree, and when one gram of hydrogen combines with 127 of iodine heat enough is absorbed to raise 6000 grams of water one degree.

When hydrogen dioxide breaks down into water and oxygen 23000 calories are set free, but it requires 68300 calories to decompose water into its constituents, hence taking the two stages of the decomposition into account the resultant energy stored up is 45300 calories.

In the combustion of methane the thermal results may be calculated as follows :— $CH_4 + 2O_2 = CO_2 + 2H_2O$. From the table above, $C + O_2 = CO_2 + 97000$ cal.
$$2H_2 + O_2 = 2H_2O + 2(68300) \text{ cal.}$$
Then $CH_4 + 2O_2 = CO_2 + 2H_2O + 233600$ cal.

Just as in mechanics a system in a stable position cannot of itself move into one of instability, but must have external energy used up in bringing about such a change ; so a chemical system (of atoms) which requires the application of external energy to cause a rearrangement of its parts (atoms) is in a condition of stability and will not of itself become unstable, that is, decomposed.

Substances that act chemically tend to form those combinations in which the greatest amount of energy is set free, hence, those that are most stable (maximum work).

CHAPTER XV.

1.—Qualitative Analysis.

Throughout the body of the book directions have been given for distinguishing the elements from one another. It is necessary, however, to know how to systematically apply tests to an unknown salt until the acid and base have been determined.

2.—Bases.

There are certain substances, known as group reagents which, when properly applied, enable the operator to divide the bases into groups, then the members of any group may be further separated into smaller divisions, until finally any particular one may be traced out.

3.—First Group Reagent.—HCl.

EXPERIMENT.

Dissolve separately some lead nitrate, silver nitrate and mercurous nitrate. (*a*) Add to each dilute hydrochloric acid. (*b*) After settling, decant most of the water and add ammonia in excess. (*c*) To some of the original solution (O.S.) add solution of bichromate of potassium, $K_2Cr_2O_7$. (*d*) Boil the three original precipitates.

Hydrochloric acid is the first group reagent and it precipitates **lead, silver** and **mercury** (ous) salts from aqueous solutions. The acid must be *dilute* when used.

4.—Second Group Reagent.--H$_2$S.

EXPERIMENT.

(*a*) Dissolve separately salts of the following metals, add hydrochloric acid, then pass into the solution hydrogen sulphide :—Copper, mercury (ic), bismuth, antimony, arsenic, tin (ous and ic), gold. (*b*) Try if the precipitate (sulphide) is soluble in ammonia or caustic potash.

The second group reagent is **hydric sulphide**, which from acid solutions precipitates the salts of

I. **Copper, mercury, bismuth, cadmium, lead.**
II. **Antimony, arsenic, tin, gold, platinum.**

The sulphides of the metals in division I. are insoluble in ammonia, those in II. are soluble.

By using a solution of the salt acidified with HCl, the metals of the first group will be eliminated, except a small trace of lead, which may appear in this group because lead chloride is very slightly soluble in water.

5.—Third Group Reagent.—(NH$_4$)$_2$S.

EXPERIMENT.

Salts of iron, aluminium, zinc, nickel, manganese and cobalt may be used. (*a*) Dissolve the salt and add ammonia, ammonium chloride and ammonium sulphide. Note the colour of the precipitates. (*b*) To some of the original solution, add ammonia or caustic potash.

The third group reagent is **ammonium sulphide** in presence of ammonium chloride in an alkaline solution.

The metals of the group are

I. **Aluminium, chromium, iron,** which form hydrates with alkaline hydroxides.

II. **Zinc, manganese, cobalt, nickel.**

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6.—Fourth Group Reagent.—$(NH_4)_2CO_3$.

EXPERIMENT.

Soluble salts of barium, calcium and strontium, may have added to them some ammonium carbonate. Test the precipitate for flame colouration.

The fourth group reagent is **ammonium carbonate. Barium, calcium, strontium,** are precipitated by it.

7.—The Fifth Group. No Reagent.

The members of this group are not precipitated by any reagent. They are **potassium, sodium, ammonium** and **magnesium.**

To sum up, there is the, **First,** the **Hydrochloric Acid** or the **Silver Group,** consisting of those metals whose **Chlorides** are insoluble.

The **Second,** the **Hydrogen Sulphide** or the **Copper Group,** made up of those metals whose sulphides are insoluble in water. The group consists of two sections, known as the **Copper** and **Arsenic** divisions. The sulphides of the former are insoluble in **ammonium hydrate,** those of the latter are soluble.

The **Third,** or **Ammonium Sulphide** or **Iron Group,** consists of those metals whose sulphides are insoluble in presence of **ammonium hydrate** and **ammonium chloride.** This group is also in two divisions, the metals of the **first** or **iron** section, have their hydrates precipitated by **ammonium hydrate.** The metals of

the **second** or **zinc** section do not form insoluble hydrates.

The **Fourth,** or **Ammonium Carbonate** or **Barium Group,** consists of metals whose carbonates are precipitated when formed in aqueous solution.

The **Fifth,** or **Potassium Group,** is made up of metals that do not form insoluble salts with any one reagent.

———

8.—Some Directions for Working in Making an Analysis.

1. Keep all vessels, brushes, stirring rods, etc., perfectly clean ; and use pure water only.

2. Examine the substance to be tested before dissolving it.

3. Keep accurate notes *made at the time* of your observations and inferences.

4. Solutions of the substances are always used for analysis, except where otherwise directed. If the salt is soluble in water, use aqueous solution for testing. If not soluble in water try first, strong hydrochloric acid; if not soluble in that use nitric acid; if not in nitric acid use *aqua regia.* The solvent may be heated in all cases. The solution thus obtained before any reagent is added is called the **original solution (O.S.).**

5. The group reagents are to be added successively to the same portion of solution unless otherwise stated.

6. Hydrochloric acid, as a group reagent, must be dilute, else it may precipitate some other metals than those of group one.

7. Always confirm results by other tests.

8. Use *small quantities* of the substance to be tested. When a reagent is to be added in excess, a few drops of the solution to be tested may be passed into another test-tube and treated separately.

9. If possible, save part of the salt unchanged, and part of the O.S. for further tests, if necessary.

9.—Examination of a Salt of a Metal for the Base.

TABLE I.—Testing for Groups.

Prepare a solution of the salt.

A. Add *dilute* HCl *in excess*. $\begin{cases}$ White precipitate. Table II.
No precipitate in excess of acid. B. $\end{cases}$

B. To same solution, add H_2S. $\begin{cases}$ Precipitate. Table III.
No precipitate. C. $\end{cases}$

C. Boil the solution to expel H_2S (or take some O.S.), add NH_4OH, and NH_4Cl $\begin{cases}$ Precipitate. Table IV.
No precipitate. D. $\end{cases}$

D. Add $(NH_4)_2S$. $\begin{cases}$ Precipitate. Table V.
No precipitate. E. $\end{cases}$

E. Add $(NH_4)_2CO_3$. $\begin{cases}$ White precipitate. Table VI.
No precipitate. Table VII. $\end{cases}$

TABLE II.—Metals of First Group.

The white precipitate has added to it some NH_4OH, then boiled if no change is apparent.	*No change*..........................**Pb**. Confirm by adding separately to O.S. some KI, $K_2Cr_2O_7$, H_2SO_4 (page 76). *Precipitate dissolved*................**Ag**. Confirm by adding HNO_3 in excess (white precipitate), and by mixing with Na_2CO_3 and reducing on charcoal. *Precipitate turns black*..........**Hg**(ous). Confirm by adding HNO_3 to part of O.S., then dip in this a bit of bright copper (grey deposit). Heat, in a tube closed at one end, with Na_2CO_3; grey deposit of Hg on tube.

TABLE III.—Metals of Second Group.

Add yellow $(NH_4)_2S$* to the precipitate.	{ Precipitate insoluble. A. { Precipitate soluble. B.

A—Copper Section of Second Group.

Precipitate, black.	Precipitate soluble in HNO_3. Solution turns splendid blue with NH_4OH.....**Cu**. Confirm by acidifying with H_2SO_4, then dip into the liquid a clean knife blade. Add to O. S. NaOH and boil; precipitate light blue, then black. Precipitate insoluble in HNO_3, soluble in aqua regia ....**Hg**(ic). Confirm by adding to O.S. some KI. Add to O.S. NaOH (yellow precipitate). Place in an acid solution a strip of copper, heat the deposit on the copper.

* Stannous sulphide SnS is soluble in alkaline persulphides, therefore there must be excess of S in the $(NH_4)_2S$.

Precipitate, black.	Precipitate partly soluble in HNO_3, dilute. . . . . **Pb.** Confirm as in Table II. Precipitate soluble in boiling HNO_3. Add NaOH to O.S. white precipitate. Add excess of water to O.S. white precipitate . . . . **Bi.** Confirm by dissolving last precipitate in HCl.
Precipitate, yellow.	Soluble in hot dilute H_2SO_4 . . . . **Cd.** Confirm by adding NH_4OH and NaOH slowly to separate parts of O.S.; white precipitate, soluble in excess.

B—Arsenic Section of Second Group.

Precipitate with H_2S, black or brown.	. . . . **Sn**(ous). Confirm by adding to O.S. slowly KOH, white precipitate soluble in excess of alkali. Add to O.S. oxalic acid, white precipitate.
Precipitate, yellow.	Soluble in NH_4OH. Turns green with am. solution of $CuSO_4$ . . . . **As.** Confirm with am. solution of $AgNO_3$ (yellow). Marsh's test with O.S. (page 89, ex. 9). White precipitate with NH_4OH. Yellow sulphide insoluble in $(NH_4)_2CO_3$ . . **Sn**(ic). Reduce to *ous* salt and confirm as above.
Precipitate, orange.	Insoluble in NH_4OH. Soluble in hot concentrated HCl . . . . **Sb.** Confirm—white precipitate with NH_4OH in O.S. Test for stibine (pages 93 and 90, ex. 6).

TABLE IV.—Metals of the Third Group.

Treat some of O.S. with KOH.

Precipitate............... ....A. Iron Section.
No precipitate...................,.......B. Zinc Section.

A—Iron Section of Third Group.

Precipitate with $(NH_4)_2S$, *black*.	Precipitate dissolved by HCl. O.S. with NaOH, gives whitish precipitate, turning green, then brown................Fe(ous). Confirm by adding to O.S. K_4FeCy_6, light blue precipitate. $K_6Fe_2Cy_{12}$, dark blue. Na_2CO_3, white, then green, then brown.
	Precipitate dissolved by HCl. O.S. with NaOH gives reddish precipitate....Fe(ic.) Confirm with K_4FeCy_6, dark blue; $K_6Fe_2Cy_{12}$, brown. KCyS, bright red.
Precipitate, *white*.	Precipitate soluble in HCl. With NaOH, O.S. gives white precipitate soluble in excess........................... ....Al. Confirm by adding to last solution HCl until acid, then NH_4OH until alkaline, (gelatinous precipitate). Heat the salt on charcoal, then moisten with $CoCl_2$ and heat again, fine blue.
Precipitate, *greenish*.	Dissolves in HCl, forming green solution ....Cr. Confirm thus,—O.S. forms greenish precipitate with NaOH, soluble in excess. Add a solution of lead salt to this (yellow precipitate).

B—Zinc Section of Third Group.

Precipitate, with (NH_4)$_2$S, *black*.

Precipitate soluble in HCl. O.S. with NaOH gives blue precipitate, insoluble in excess, soluble in NH_4OH..............**Co.**
Confirm. Borax bead turns blue when Co is dissolved in it. O.S. gives green precipitate with K_4FeCy_6, reddish precipitate with $K_6Fe_2Cy_{12}$, both insoluble in HCl.

Precipitate soluble in HCl, greenish precipitate with NaOH, insoluble in excess. Soluble in NH_4OH..................**Ni.**
Confirm. K_4FeCy_6 in O.S. forms greenish precipitate. Na_2CO_3 gives greenish precipitate. With borax it forms violet bead in O.fl. when hot.

Precipitate with (NH_4)$_2$S, *white*.

Precipitate soluble in HCl, insoluble in $HC_2H_3O_2$ . . ..**Zn.**
Confirm. O.S. yields white precipitate with alkaline hydrate, soluble in excess. Na_2CO_3 in O.S. forms white precipitate soluble in NH_4OH.

Precipitate with (NH_4)$_2$S, *pink*.

With NaOH, O.S. gives white precipitate, becoming brown in air, soluble in NH_4Cl
....**Mn.**
Confirm thus,—heat sal K_2CO_3 and KNO_3. It turns gr   Borax bead with salt, amethyst when hot, reddish when cold after heating in O.fl.

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TABLE V.—Metals of the Fourth Group.

With $(NH_4)_2CO_3$ white Precipitate.	
	Add $CaSO_4$ to O.S., white precipitate *at once*...............................**Ba.** Confirm by adding acetic acid and $K_2Cr_2O_7$ to O.S., yellow by flame test (page 35, ex. 1).
	Precipitate with $CaSO_4$ forms slowly...**Sr.** Confirm by flame test (page 34, ex. 1).
	With $CaSO_4$, no precipitate.........**Ca.** Confirm thus,—$(NH_4)_2C_2O_4$ gives white precipitate with O.S. Ca gives orange-red colour to flame (page 31, ex. 1).

TABLE VI.—Metals of the Fifth Group.

Salt on platinum loop colours the flame crimson...........................**Li.**
Confirm by treating concentrated O.S. with Na_2CO_3, white precipitate.

Salt on platinum loop colours flame bright yellow.............................**Na.**

Salt on platinum loop colours the flame violet.........   ....**K.**
Confirm by testing with tartaric acid (white precipitate).

O.S. gives white precipitate with Na_2CO_3 ....**Mg.**
Confirm by treating O.S. with $Ca(OH)_2$, white precipitate. Also with $(NH_4)_2HPO_4$ or Na_2HPO_4 in presence of NH_4OH (white precipitate).

Solution heated with KOH gives off ammonia . ...**NH₄.**
Confirm by Nessler's test.

To test for the more commonly occurring acid radicals in salts containing one acid :—

First Group......Reagent, **Barium Nitrate.**

This reagent forms a white precipitate with a sulphate, carbonate, oxalate, silicate, phosphate, borate and sulphite.

Second Group......Reagent, **Silver Nitrate.**

With silver nitrate a precipitate is formed by a chloride, bromide, iodide, cyanide, sulphide, nitrite, and thiosulphate (hyposulphite).

Third Group......No general reagent.

This group may contain a chlorate, nitrate, tartrate, or acetate.

To test for the acid, make a solution of the salt. Add solution of $Ba(NO_3)_2$.* If no precipitate appears at once, let the mixture stand for a few minutes.

White Precipitate........................Table I.
No Precipitate. Add $AgNO_3$ to O.S.
Precipitate............................... Table II.
No Precipitate............................Table III.

TABLE I.

Shake up a little of the precipitate with water and add HCl. Observe if a gas is given off, if so test it with $Ca(HO)_2$.

A—White precipitate not dissolved........... **A Sulphate.**
      Confirm by heating the salt with Na_2CO_3
      on charcoal in reducing flame, then apply-
      ing test with silver.

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* After dissolving the nitrate of barium, add nitric acid until no more precipitate is formed, then filter and use the clear solution as the reagent.

B—Precipitate dissolved.

Add H_2SO_4, and heat, if necessary.

(1) CO_2 given off. (It was also given off when HCl was added) .... **A Carbonate.**
Confirm by adding HCl to the salt, then passing gas into $Ca(OH)_2$.

(2) SO_2 given off....................... **A Sulphite.**
Confirm by adding $AgNO_3$ to O.S. White precipitate, Ag_2SO_3, turns dark on heating.

(3) CO and CO_2 given off................. **An Oxalate.**
Confirm by adding $CaCl_2$ to O.S. White precipitate, soluble in HCl, insoluble in $HC_2H_3O_2$. If this precipitate be heated just to redness it effervesces with HCl.

O.S. with $AgNo_3$ gives white precipitate, soluble in HNO_3.

O.S. with stannous chloride gives white precipitate.

(4) A deposit of Silica separates............ **A Silicate.**
Confirm by heating a *little* of the powder in Na_2CO_3 on platinum loop, when a colourless glassy bead is formed with evolution of CO_2.

(5) No apparent change.
Test O.S. with $AgNO_3$.

(6) A yellow precipitate.................. **A Phosphate.**
Confirm with ammonic molybdate.

(7) A brownish precipitate............... **A Borate.**
Confirm by flame test (page 54).

TABLE II.

Group reagent—**AgNO₃**.

A solution of the salt, with silver nitrate added, gives

A—A white precipitate.

Add H_2SO_4 to O.S. and heat.

(1) Hydrochloric acid gas given off . . . .**A Chloride.**
Confirm by testing for chlorine with
H_2SO_4 and MnO_2.

(2) SO_2 and S separated. . . . .**A Thiosulphate.**
Confirm by adding any other strong acid
to O.S.

(3) Nitrous fumes (reddish) given off. . . . . . .**A Nitrite.**
Confirm by adding some O.S. to a little
solution of $KMnO_4$ acidified with H_2SO_4,
also by adding to O.S. some starch paste
and KI.

B—A yellowish white precipitate.

Add H_2SO_4 to O.S. and heat.

(1) Red fumes of bromine given off. . . . .**A Bromide.**
Confirm by adding Cl solution to O.S.
with starch.

(2) Violet vapours of iodine. . . . .**An Iodide.**
Confirm by adding solution of a lead salt
or of mercuric chloride to O.S. ; also by
adding Cl to O.S. with starch.

C—A black precipitate.

Add H_2SO_4.

(1) H_2S given off . . . .**A Sulphide.**
Confirm by silver test.

TABLE III.

No precipitate with $Ba(NO_3)_2$ or $AgNO_3$.

Add H_2SO_4 to a *little* of the solid, and heat, if necessary.

(1) Brownish acid fumes.................. **A Nitrate.**
Confirm by treating solution with H_2SO_4 and $FeSO_4$.

(2) Colourless acid vapour, with smell of vinegar........................... **An Acetate.**
Confirm by neutralizing the solution of the salt, then adding Fe_2Cl_6, this gives bright red colour without precipitate.

(3) A yellow gas that explodes in air........ **A Chlorate.**
Confirm by heating for free oxygen and a chloride.

(4) Mixture turns black or brown.......... **A Tartrate.**
Confirm by adding slowly K_2CO_3 with constant stirring, white precipitate. Repeat, using ammonia. In both cases the solution must be acid.

SELECTED QUESTIONS.

The following questions are selected from examination papers on the work covered by this book :—

1. One gram of a certain metal when dissolved in dilute sulphuric acid, liberates 200 c.c. of hydrogen gas. Find the combining weight of the metal.

2. By what experiments would you distinguish marsh gas and olefiant gas ?

5 c.c. of a mixture of marsh gas and olefiant gas are exploded with 14 c.c. of oxygen : 9 c.c. of gas remain, of which 7 c.c. are

absorbed by caustic potash.　Find the volume of each of the gases in the original mixture.

3. (*a*) How would you prove that the gas obtained by pouring sulphuric acid upon ferrous sulphide contains both S and H ?

> (*b*) A solid substance contains both a carbonate and an easily dissolved sulphide.　How would you prove the presence of these two bodies ?

> (*c*) A piece of sodium was completely converted into chloride by uniting with 200 c.c. of Cl at the standard temperature and pressure.　What was the weight of the sodium ?

4. State Avogadro's hypothesis and give the evidence in support of it.　Deduce the general statement that if M be the density (Hydrogen $= 1$) of any substance in the gaseous state, M grams of that substance in the gaseous state will occupy approximately 11.16 litres at 0°C. and 760$^{mm.}$ Bar.

5. 0.6 grams of a certain metal when dissolved in dilute sulphuric acid liberates 558 c.c. of hydrogen at 0°C. and 760$^{mm.}$ Bar. A determination of its specific heat gave .25.　Find the atomic weight of the metal.

6. (*a*) Describe experiments illustrating the difference between (i) nascent hydrogen and hydrogen, (ii) nascent oxygen and oxygen.

> (*b*) Write equations illustrating the action of nascent hydrogen upon (i) nitric acid, (ii) solution of arsenious oxide, (iii) nitric oxide.

7. Describe experiments illustrating how you would detect

> (*a*) Potassium nitrite in presence of potassium nitrate ;
> (*b*) Potassium sulphite in presence of potassium sulphate ;
> (*c*) Potassium chloride in presence of potassium bromide ;
> (*d*) Arsenic hydride in presence of antimony hydride.

8. (*a*) How much oxalic acid ($C_2H_2O_4$) must be heated with sulphuric acid to prepare 145 litres of carbon monoxide at 17°C. and 800$^{mm.}$ Bar.

> (*b*) Explain what occurs when a mixture of carbon monoxide and chlorine is exposed to sunlight and the product shaken up with water.

(c) If 100 c.c. of a mixture of carbon monoxide and hydrogen gas were given you for analysis, describe how you would proceed to determine the volume of each gas in the mixture.

9. Describe, giving equations, what will occur in each of the following experiments :—

(a) A piece of yellow phosphorus is suspended in Chlorine in a bottle.

(b) The product of reaction (a) is shaken up with water.

(c) An electric spark is passed through the air in a closed flask containing also a small quantity of a solution of potassium iodide.

(d) Hydrochloric acid is added to a few crystals of potassium chlorate in a bottle and hydrogen sulphide is then passed into the bottle.

(e) Lead nitrate is heated and the gas given off is gradually cooled down to −20°C.

10. Describe the relations which sodium and its compounds bear to potassium and its compounds.

11. (a) In the periodic arrangement of the elements, manganese is placed in the same group as chlorine. Write the formulæ of the compounds of these elements that illustrate this relation.

(b) Write equations showing the action of (i) concentrated sulphuric acid on manganese dioxide, and (ii) dilute sulphuric acid and potassium permanganate on ferrous sulphate.

12. (a) The specific gravity of hydrogen is 0.0692, that of ammonia is 0.595 (air = 1). What is the molecular weight of ammonia? Explain how you arrive at your conclusion.

(b) The vapour density of sulphur is said to be abnormal at 500°C. and normal at 1000°C. Explain the meaning of these statements.

(c) Describe experiments to show that ammonium chloride is decomposed by heat into ammonia and hydrogen chloride gas.

13. A gas gives, on analysis,

$$
\begin{array}{ll}
\text{Carbon} & = \quad 85.78 \\
\text{Hydrogen} & = \quad 14.32 \\
\hline
& \quad 100.
\end{array}
$$

300 c.c. of the gas at $10°$C. and 750 mm. Bar. weigh 0.35 grams.   Write the formula of the gas.

14. (*a*) How can barium oxide be used as a means of preparing oxygen from the air?

(*b*) Compare the chemical properties of oxygen and ozone.

(*c*) If the molecule of oxygen consists of two atoms, then the molecule of ozone consists of more than two atoms. State facts in support of this statement.

15. Chlorine, bromine and iodine are said to belong to the same natural family of elements.   Explain and illustrate this statement.

16. (*a*) How could you prepare the trihydride of arsenic (arsine)? Compare its properties with ammonia and phosphine.

(*b*) Write equations showing the reactions which occur when arsine, phosphine, and ammonia respectively burn in air.

17. Write equations illustrating the action of hydrogen sulphide upon :

(*a*) Chlorine gas.
(*b*) Ammonium hydrate.
(*c*) Nitric acid.
(*d*) Antimonous chloride.
(*e*) Solution of ferric chloride.

18. A solution is known to contain silver nitrate, ferrous nitrate, ferric nitrate or arsenious oxide.   How would you determine which it contains?

19. (*a*) Give an account of the chemistry of calcium.   Illustrate its relations to barium and strontium.

(*b*) What is the cause of the so-called temporary hardness of water?   Explain the chemical reactions which occur in the different methods adopted for its removal.

20. (*a*) " The temperature of a burning match is far above that of a red hot iron poker." Describe an experiment which proves the correctness of the statement.

(*b*) What volume, calculated at standard temperature and pressure, will be occupied by the products of the combustion in oxygen of one gram of each of the following substances : ammonia, phosphoretted hydrogen, carbon disulphide, and arsenic ?

21. Dalton's analysis of two compounds yielded the following results:

| Carbon | - | 42.86. | Carbon | - | 27.27. |
| Oxygen | - | 57.14. | Oxygen | - | 72.73. |

Show the relation of these data to (*a*) the relative (or proportional) weights of these elements, (*b*) the law of multiple proportion, and (*c*) the atomic theory.

22. Find the atomic weights of the elements from the following data :

(*a*) A gram of a certain metal dissolved in dilute sulphuric acid yielded 344 c.c. of hydrogen at standard temperature and pressure. Its specific heat was found to be ·0956.

(*b*) 35·5 parts of chlorine unite with 100 parts of mercury to form mercurous chloride, and with 200 to form mercuric chloride. The specific heat of mercury is 0·32.

23. (*a*) Make a solution of barium nitrate ; add to it, drop by drop, a solution of sodic carbonate until no further precipitate forms ; filter off the liquid portion ; collect, dry and heat precipitate just to redness ; add hydrochloric acid until all action ceases ; dip a platinum wire into the solution which forms and place in the non-luminous flame of a Bunsen burner. Explain the whole series of changes and phenomena. Give equations.

(*b*) What other metals exhibit a similar series of changes under somewhat similar conditions ?

24. (*a*) You are furnished with sulphate of magnesia and all necessary reagents and apparatus. Describe how you

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would prepare the oxide, the chloride, and the carbonate
of magnesia.

(*b*) Of what other elements could you form similar compounds
in a somewhat similar manner ?

25. Sketch the chemistry of sodium.

26. Give a practical definition of a dibasic acid.   Name one,
write its formula, and show how your definition applies to the acid.

27. The vapour density of hydriodic acid is 4.43 (air = 1) ; that of
phosphorus tri-iodide is 14.27 ; the percentage weight of iodine in
these compounds is respectively 99.2 and 92.5.   Calculate the
atomic weight of iodine.

28. Compare the hydrides of the members of the nitrogen group.

29. (*a*) Two-tenths of a gram of a compound having the com-
position $C_{12}H_{22}O_{11}$ is burnt in air.   Explain the chemi-
cal changes that take place, using equations.   Calculate
the products of the volume of the products of combustion
at 100°C. and 740 mm.

(*b*) .18 gram of a compound containing carbon, hydrogen
and oxygen, yields, on analysis, .072 gram of carbon,
.012 gram of hydrogen, .096 gram of oxygen.   Calculate
the simplest formula of the substance.

30. Define the terms "oxidizing agent" and "reducing agent,"
and illustrate your definitions by reference to the experiments :—

(*a*) Sulphuretted hydrogen gas is passed into a solution of
ferric chloride.

(*b*) Carbon is heated to a high temperature with ferric oxide.

(*c*) Sulphur dioxide is passed into a solution of permanganate
of potash.   Give equations.

31. (*a*) Dalton's gravimetric analysis of two compounds yielded
the following results :—

Nitrogen 63.64   Nitrogen 46.67.
Oxygen   36.36   Oxygen   53.33.

Show the relation of these data to Dalton's formulæ for
these substances (NO and NO_2).

(b) Gay Lussac's volumetric analysis of the mixture resulting from the decomposition of these same compounds gave the following results :—

Nitrogen 66⅔ vols.   Nitrogen 50 vols.

Oxygen   33⅓ vols.   Oxygen   50 vols.

Show the relation of these data to the present formulæ for these substances, and to Avogadro's law.

32. (a) Describe what takes place when :

(i) Iron is immersed in a solution of sulphate of copper.

(ii) Copper, in a solution of bichloride of mercury.

(iii) Zinc, in a solution of acetate of lead.

(iv) Magnesium, in a solution of nitrate of silver.

(b) Explain how quantitative results in these experiments can be used as an aid in determining atomic weights.

33. Describe simple laboratory methods of preparing small quantities of (a) metallic arsenic from the trioxide, (b) trichloride of antimony, (c) ferrous sulphate.

34. Sketch the chemistry of lead.

35. What is meant by the " Periodic Law"? Illustrate its significance by reference to the members of group iv. (Carbon $=12$, silicon $= 28$, tin $= 118$, lead $= 207$.)

36. The average composition of coal gas is : hydrogen, 45% ; methane, 35% ; carbon monoxide, 7% ; olefiant gas, 4% ; butylene (C_4H_8), 2.4% ; sulphuretted hydrogen 0.3% ; nitrogen 2.5% ; carbon dioxide, 3.8%. What volume will the products of the combustion of 100 litres of such a gas occupy at $20°C$. and 750 mm. pressure ?

37. Explain, using equations, what changes take place in the following experiments :—

(a) Dry sulphuretted hydrogen is passed over iron filings in a glass tube.

(b) Sulphur dioxide is passed into a vessel containing nitrogen peroxide.

(c) Carbon dioxide is passed over ignited sodium.

38. Ferrous sulphide (FeS) is heated strongly in a hard glass tube open at both ends. Express the reaction which takes place by an equation.

39. (*a*) When 50 c.c. of hydrogen and 30 c.c. of chlorine are exploded in a eudiometer, what are the volume and the composition of the resulting gas at standard temperature and pressure?

(*b*) 50 c.c. of hydrochloric acid gas are placed in a eudiometer over mercury ; some sodium amalgam is then introduced and the lower end of the tube is firmly closed with the finger, and the whole inverted a number of times so that the gas may come freely into contact with the amalgam. The tube is again inverted over mercury and the volume measured. What changes have taken place? Explain.

(*c*) Show the relation of these experiments to the statement that "hydrogen is represented by the symbol H_2."

40. Sketch the chemistry of iodine.

41. How could small quantities of arsenic, iron, lead, sulphur, silicon, iodine, be prepared, as laboratory experiments?

42. 500 c.c. of a solution of sodic hydrate, containing 30 grams of hydrate per litre of solution, is required to neutralize 100 c.c. of sulphuric acid. Find the quantity of pure acid per litre.

43. Hydriodic acid gas is collected in several vessels, and steam is led into one, chlorine into a second, ozone into a third, and ammonia into a fourth, electric sparks from an induction coil are passed through a fifth. Describe, with equations, the changes in each case.

44. How are lead, arsenic, iron, aluminium obtained from their oxides?

45. A chemist wished to find the strength of some solution of silver nitrate. He first determined its sp. gr. as 1.08 ; then he took 10 c.c. of it and added excess of NaCl solution. Afterwards he filtered the mixture, dried the solid and weighed it. The weight was .84 gram. Calculate the percentage strength of the nitrate solution.

46. A quantity of caustic soda solution is dissolved and divided into four parts. Into one water is poured, then there is passed some chlorine gas through it. Into a second, which has been boiled to concentrate the solution, some chlorine gas is also passed. Bismuth nitrate is added to a third, ferric chloride solution is mixed with the fourth. Write the equations for the chemical reactions.

47. Oxygen and sulphur belong to the same chemical group. Why?

48. If tin sulphide were given, how could the metal be obtained? What would be the result of adding a solution of stannous chloride to one of ferric chloride? If peroxide of lead were shaken up with a solution of stannous chloride, what would take place?

49. Manganese dioxide is heated with potassium nitrate, the resulting compound is thrown into a strong solution of carbon dioxide in water. Some stannous oxide is then shaken up with the mixture. Trace the changes.

50. Potassium ferrocyanide is (*a*) strongly heated, (*b*) heated with concentrated sulphuric acid, (*c*) heated with dilute sulphuric acid, (*d*) mixed with a solution of a ferric salt. What are the resultant compounds?

51. Show the resemblances between the compounds of sulphur and oxygen by (*a*) comparing similar combinations, (*b*) by pointing out displacements of one by the other in compounds.

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